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REFINER
AND NATURAL GASOLINE MANUFACTURER

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The Look Box

Metallurgy

THIS month, and next month, The Refiner devotes its pages to the presentation of a symposium on the metallurgy of petroleum refining equipment. To this important work a number of leading metallurgists and technologists of both the oil refining and steel industries have contributed articles of real value. The purpose of the symposium on progress in metallurgy is primarily one of bringing down to date all metallurgical information presently available which pertains to metallic equipment in petroleum refining processes.

The present symposium is a sequel to the original Metallurgical Symposium published in the April and May issues of 1933. The first symposium consisted of 15 papers by well known authorities in many fields of metallurgy in the steel and oil refining industries. This major editorial work was well received, and despite a large overprinting of the two issues, all copies were quickly distributed. It marked the first correlation of metallurgical technology in this field, and as such filled a definite need.

The second symposium now being presented correlates and brings down to date metallurgical information now available, placing review of the latest developments in two volumes handily accessible to readers. This important data, presented in this manner, will prove of real and lasting value, for nowhere else in petroleum literature has modern technique and engineering information along with scientific metallurgical data been brought together for handy reference and study. Progress and development in metallurgy has been rapid during the four years since publication of the original metallurgical symposium by The Refiner. Scattered publication of data in various journals has not been nearly sufficient to guide the industry nor to make known to it the advanced materials available and their proper application to a multitude of requirements.

During the past four or five years, refiners and steel manufacturers have done a vast amount of experimenting and development work in the application of various alloy steels. Unsatisfactory experience has been reported in some instances. As usual with new materials of construction, a great deal of exchange of information and co-

operation between refiners and steel and other manufacturers has been necessary to further the development of both materials and processes. As a result, the refining industry now has a considerable number of reliable alloys for use and with accurate knowledge as to their usability for given services. Because of increased knowledge and care on the part of both user and manufacturer, many of the alloys now are definitely out of the experimental class. Further information is required regarding the proper use and application of many more of the available materials. Much of such information is presented in the contributions to this symposium.

Because of the often severe conditions of temperature, pressure and corrosion in the petroleum refining industry, the demand for alloy steels has been steadily increasing during recent years. The severity of service requirements is not equalled in any other industry. Engineers and metallurgists in both the refining and steel industries are to be complimented on the thoroughness of their co-operative study and the success attained in the solution of the many problems with which they have been confronted. Much yet remains to be done. New developments of importance are being announced periodically as the work progresses. Much new data are presented in the present symposium, new thoughts advanced, processes discussed, and experience records detailed.

In regard to the various discussions presented, THE REFINER calls attention to the fact here that the statements and the opinions expressed therein are strictly those of the authors and should not be construed as the opinion or as an endorsement of this journal. The symposium contains an unusual amount of information, thanks to the co-operation of the various experts who have prepared the papers interpreting their views and experiences as seemed best for the proper correlation of the scientific data at hand. In many instances the material presented in this symposium is based on the work of members of the American Society of Mechanical Engineers, the American Society for Testing Materials, the American Chemical Society, the American Society for Metals, the American Petroleum Institute, and the American Institute of Mining and Metallurgical Engineers. All of these bodies have been active during recent months especially in metallurgical investigations, and all of this activity is but indicative of the present marked interest in this major problem of perfection and selection of metals best suited for the industry's requirements.

Selection and applicability of many alloys and metals is discussed in the group of articles comprising this symposium. The contributors discuss such equipment as polymerization and cracking-still tubes, fractionating columns, furnaces, tube supports, return bends and headers, reaction chambers and other pressure vessels, transfer lines, pipe and pipe connections to reaction chambers, vapor lines, liquid-level lines, hot-oil and pressure-distillate pumps, the liquid ends and surge blocks of pumps, and pump liners, castings, impellers, piston rods, shafts, pump valves, and nuts and bolts for hot-oil pumps. Also the discussions include valve bodies and valve trimmings, plugs, flanges, compressors, compressor cylinders, pistons, piston rings, cylinder heads and cylinder linings. Accumulators, run-down tanks, general piping, bubble caps, dephlegmators are discussed as is tubing for preheaters, condensers, reboilers, after-cooler, heat exchangers, surface condensers and other shell-and-tube equipment. The list is but typical of the hundreds of items of equipment and equipment parts which must be given consideration in supplying the metals required for the modern efficient petroleum refinery or natural gasoline plant.

The discussions presented at this time are comprised of the thoughts and knowledge of the individual contributors, based on the author's experience and available information. Nothing final is attempted. The field of metallurgy is progressing rapidly. Since the discussions are packed with useful and timely information, designers are provided with useful information in usable form. Here engineers may learn how best to employ the stainless steels and irons, the nickel and nickel alloys, the newer cast irons, the many alloys of chrome, nickel, vanadium, molybdenum, tungsten, manganese, silicon, aluminum, copper, and so on, which have been perfected, tested, improved, and are in successful commercial use. As the scientific knowledge piles up, coming as it does from a larger number of industries, much further progress in development will come through the "borrowing" process. A large part of this progress will be contributed by the petroleum refining industry.

THE Oil Corrosion Problem

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THE corrosion of metals is one of the world's most vital and important problems, and is the most difficult to solve from the economic and technical standpoint. One may say, in general, that practically no type corrosion is insurmountable—but the price is prohibitive at the moment.

Every metal under commercial use will corrode. Rusting of iron, the outstanding structural material, is the foremost problem in corrosion. The destructive forces of corrosion are ever present regardless of where iron or steel is used. The world's corrosion bill is tremendous and the mere cost of replacement of metals is an economic waste which yearly costs the world over two billion dollars, of which the losses in the United States are over a billion dollars. The corrosion invoice for the oil industry throughout the world was of the order of 250 million dollars for the year 1936.

By reason of the range and variety of its operations, the oil industry is in a peculiarly unfavorable position as regards corrosion. There is scarcely a form which it takes that is not encountered in handling crude oil. The spheres of petroleum production, transportation, storage, refining, and utilization must combat its own corrosion problems.

The damage by corrosion continues despite earnest endeavors to solve the many problems involved. The workers engaged in the study of corrosion are numbered by thousands. The theories which have been advanced to account for the rusting of iron alone would fill volumes. To combat corrosion, every resource of science and technology has been called upon. The metallurgist has been a leader in the battle to eliminate or modify the rate of corrosion as a function of metals and its alloys. They have made great strides in solving the problem, but much is yet to be done—which can only result from research of a fundamental and utilitarian character. Remedies by the score have been proposed; alloy steels containing chromium, nickel, molybdenum, aluminum, tungsten, silicon, copper, ceremic coatings, paints, metallic spray, and bituminous coverings, are but a few of the remedies which have been used with some success.

High-priced alloys resist corrosion in some phases of the industry and last a long time; however, the rapid rate of obsolescence in the oil industry makes the replacement of all equipment with alloys not only an enormous expense, but one which is needless in view of the rapidly changing equipment design in many cases.

From the time that drilling for oil starts, clear to the use of gasoline in motor cars, corrosion of all types is present.

Corrosion, in production equipment, casing, and gathering lines, is caused by chemical and electrolytic action of the soil, underground waters, and compounds present in the crude oils such as hydrogen sulfide. In contrast to refinery corrosion, the production equipment is acted upon at ordinary temperatures while refinery practice must combat it at low and high temperatures.

Saline or acid waters, hydrogen sulfide, or other forms of sulfur cause the most severe corrosion on production equipment and wherever these are found the replacement costs are high. Casing failure has two bad features, not only does it call for replacement, but when water is allowed to pass into the casing, it impairs the value of the well and emulsifies the oil. This calls for subsequent treatment which adds to refining difficulties due to hydrolysis of magnesium chloride or other salts producing corrosive hydrochloric acid calling for neutralization with costly chemicals such as ammonia. The salts present in the water, deposit on the heating element of the crude distillation or cracking unit.

The corrosion of casings of wells occurs both internally and externally. Ground waters and moist soil in many cases are strong electrolytes, which act both chemically and electrolytically, causing external corrosion. Electrolytic corrosion is potentially present since a current may be set up between the soil and tube, on different sections of the tube where films were formed, and between the water layers of two different salt concentrations. Internally, corrosion is caused by water accompanying the oil, air, or hydrogen sulfide. Electrolytic decomposition may also start between the tube and films because the saline or acid water and hydrogen sulfide present are good conductors.

Casing is not the only piece of production equipment which corrodes under service in the field, strainers, valves, sucker rods, flow lines, lead lines,

rings and storage tanks are in contact with all the materials causing corrosion.

Gathering and lateral lines are subjected to heavy corrosion primarily due to the fact that the lines are laid through and over salt water drainage areas. Much of the corrosion difficulties could be eliminated by use of protective materials where most of the corrosive waters are in contact with the pipe line. Protective measures have been derived from alloys, special coatings, such as aluminum, plastics, bitumenic material, cements, but the problem still remains, as no one method of tubing protection is satisfactory in all cases due to the manifold differences in corrosive materials to which the tubes are subjected.

Acidizing of wells by hydrochloric acid has increased the hazards of corrosion not alone in wells and pipe line equipment but also refineries. Part of the hydrochloric acid is neutralized by ammonia, however, since it reacts with the oil or forms salts with the lime formation which are suspended in the crude oil, which gives difficulties in distillation or cracking equipment.

In general, pipe line corrosion is due to external causes; however, much internal corrosion takes place due to the moisture, emulsified water, hydrogen sulfide, oxygen, and other components present in the oil and gas. There are over 200,000 miles of pipe lines for the transportation of oil and natural gas. It has been estimated that the annual loss by corrosion averages approximately $300 per mile of pipe line.

A particularly interesting research on natural gas transmission lines was conducted by the United States Bureau of Mines, who found that corrosion in natural gas lines may be due to only traces of hydrogen sulfide, i.e., 12 grains or less per 100 cubic feet of gas. As a part of this work, a transmission line operating at 300 pounds, transporting gas which contained 2 grains or less of hydrogen sulfide per 1,000 cubic feet was studied. Within the last few years several failures have occurred in this line as a result of the thinning of the walls of the pipe.

Internal corrosion of transmission and distribution lines by hydrogen sulfide may be minimized by cement lining the pipe or adding protective films such as lacquers, tars, oils, etc. Corrosion-resisting alloys or metals appear to be too expensive at the moment to use for pipe lines and seem to be limited to use as lining of the pipes with a thin layer of high chrome-steel alloy and aluminum foil.

Many methods have been tested in order to safeguard tanks from corrosion, such as cementing, lining with aluminum or aluminum structure entirely, or coating with lacquers, bitumenic material, with considerable success but the problem is still with us.

Refinery equipment whether at very low temperatures in dewaxing oils at minus 60° F., or cracking temperatures to over 1100° F., has called for new and improved alloys in order to withstand the new-temperature-pressure conditions desired in processing oil for modern lubricants and gasolines.

Probably no more serious factor in corrosion as it affects the oil industry exists than that present in distillation and in cracking equipment in refineries. Corrosive crudes attack almost every part of atmospheric or cracking installations which calls for expensive protective measures or frequent replacement. There is not alone the great monetary loss involved due to expensive alloys but also the high danger of failure of the corroded equipment, bringing about loss of life and fire.

The corrosion of refinery equipment is mainly due to the action of hydrogen sulfide and hydrochloric acid. Hydrogen sulfide gas is dissolved in many crude oils as produced and a greater amount is produced by the cracking of the sulfur compounds in the charging stock. Since the acidizing of wells, apparently an increased content of salts are suspended in the crudes, with the result that they not alone deposit upon the heater tubes, but also act catalytically in producing increased amounts of hydrogen sulfide. Hydrogen sulfide not alone reacts with metals but deposits pyrophoric scale in the inside of distillation equipment which when air contacts therewith may burst into flame.

The amount of hydrogen sulfide formation is not a function of the percentage of sulfur in the original charging stock, since some relatively low sulfur-containing stocks have a higher corrosion rate than one which may contain more than twice as much sulfur.

There are two distinct differences in the action of hydrogen sulfide and hydrogen chloride as corrosive agents. Hydrogen chloride results from hydrolysis of water present in crude oil and appears early in the distillation of the crude. In the absence of water it is, as far as we know, harmless but in the cooler portions of the systems where water condenses, the hydrogen chloride dissolves therein forming hydrochloric acid which is highly corrosive unless combined with a chemical agent such as ammonia or caustic soda. The "hydrochloric acid corrosion zone" includes the heat exchanger, condensers, rundown lines, particularly in places where water may be trapped as around valves and horizontal lines. Some rundown lines have corroded away in 48 hours of use.

Hydrogen sulfide, on the other hand, evolves in many cases throughout the entire course of distillation. Its formation rate depends upon the type of oil distilled and the manner in which the sulfur compounds in the stock break down under thermal conditions. The corrosive effect of hydrogen sulfide manifests itself usually to greatest degree in the hottest portions of the system. The greatest danger due to hydrogen sulfide lies in the high-temperature zone such as flash tubes, reaction chamber, flash chamber, vapor lines, bubble towers, hot-oil pumps, in addition to return bends, plugs, pyrometer wells. With mild steel, reaction chambers have been known to corrode away at the rate of one sixteenth of an inch per month.

There is no question but that alloy steels can be fabricated to withstand the corrosive conditions in the oil industry, but at a relatively high price. In some cases these high-priced alloys have resisted corrosion. It is the task of the metallurgist to develop new alloys so as to cut the cost of combatting corrosion in the oil industry.

Many methods have been used to combat refinery corrosion such as injection of chemicals, alloy steels, calorized tubes, and cements or sprayed metal liners for reaction chambers.

New alloys of proper physical and chemical properties are continually being developed by the metallurgists, and it is hoped that from fundamental researches low-priced alloys will be found to do the job that the high-priced ones of today are accomplishing in the oil industry.

Nickel-Bearing Alloys *for Refinery Service*

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TECHNOLOGISTS associated with refineries have performed unbelievable feats in developing the petroleum products now generally on the market. For instance, they can dip into the murky depths of a crude oil and remove therefrom only the fraction useful as a lubricant. By additional action the last traces of asphalt can be rejected from this fraction and likewise undesirable paraffins.

In applying their magic these technicians often find themselves confronted with the problem supposedly presented to the inventor of a universal solvent, namely, to find a vessel to contain the solvent and solution. It is at this point that the help of the metallurgist is solicited and it is not surprising that an able staff of metallurgists is associated with the petroleum refining industry. These metallurgists must be acquainted with the chemical and physical properties of most of the ferrous alloys; also with a large number of non-ferrous alloys and with the current advances in the art and science of the control of corrosion.

Sub-zero temperatures are used in refineries during dewaxing of lubricating oils and in modifying the selective action of solvents. The 2.25-2.75-percent nickel-bearing steels occupy an enviable position as the material from which large vessels are formed for use at (—50° F. and —75° F.) temperatures. The suitability of the 2.25-2.75 percent nickel steel for this use is based on ease of fabrication, satisfactory weldability and a retention in both plate and weld of a high degree of the room temperature impact value at —50° F. The use of this nickel steel for low temperature service has been

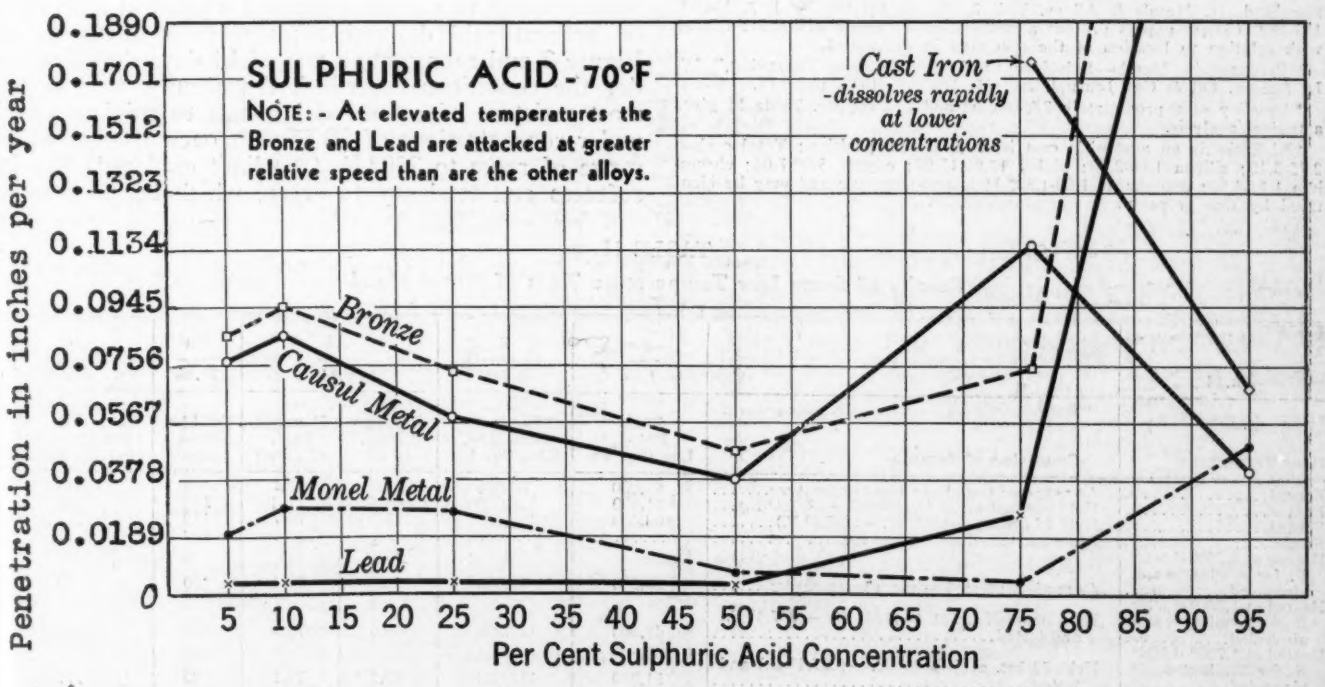


FIGURE 1

Corrosion rates of value construction materials in sulphuric acid solution at 70° F. (Lunkenheimer Company) "Causul metal" is a specific grade of alloy of the Ni-Resist type.

TABLE I

Impact Values of Some Cast Nickel Steels at Sub-Zero Temperatures

SYMBOL	COMPOSITION				U.T.S. Lbs./ Sq. In.	Y.P. Lbs./ Sq. In.	El. in 2" Percent	R.A. Percent	CHARPY IMPACT (Keyhole Notch)		
	Carbon	Manganese	Silicon	Nickel					Room Ft. Lbs.	−50° F. Ft. Lbs.	−75° F. Ft. Lbs.
A	0.24	0.62	0.42	2.39	81,700	61,500	32.0	53.5	29	23 —22	19 —18½
A1	A plus 1¼ lbs. Aluminum p. ton in ladle				82,500	64,000	29.0	45	21	14½—15¼	12½—15½
B	0.30	0.68	0.38	3.14	85,000	64,000	31.0	58.5	33	21½—22	19 —20½
B1	B plus 1¼ lbs. Aluminum p. ton in ladle				85,000	65,300	28.5	47.5	26	15½—15¼	13½—11½
C	0.17	0.63	0.34	2.57	76,000	54,000	32.0	62.5	29	24½—22½	22 —19½
C	....	....	....	....	.....	.....	....	....		42—51¼ Charpy V Notch	
C	....	....	....	....	.....	.....	....	....		46—46½ Charpy V Notch	
Ni-Mo Steel	0.24	0.64	0.33	2.15 (0.33Mo)	89,000	68,000	25.0	53.0	35—36½	26½—27	23½—22½

Heat Treatment A, B, C (1" Specimens).....Heat to 1700° F.—Cool in Air
Heat to 1525° F.—Cool in Air
Draw at 1200° F.—Cool in Air

Heat Treatment Ni-Mo Steel.....Heat to 1850° F.—Cool in Air
Heat to 1525° F.—Cool in Air
Draw at 1200° F.—Cool in Air

well covered in the literature [1,2,3]. The behavior of cast nickel steels at low temperatures has recently come in for intensive study and some results are reported in Table I. The study of steels A, B and C in this table shows that treating with aluminum tends to lower the impact values both at room and sub-zero temperatures in the case of cast steels.. The opposite is true in the case of wrought nickel steels where the impact value is improved by the use of aluminum.

The 2.5-3.5 percent nickel cast steels are finding wide application as valve bodies and parts, pump parts, fittings, and as exchanger shells and heads.

The effect of sub-zero temperatures upon Monel* is that the physical properties are improved while the impact value remains substantially the same down to liquid air temperatures (—) 183° C. or (—) 297.4° F. as obtained at room temperatures. This is shown in Table II. The above appears also to be true for the austenic 18 percent chromium 8 percent nickel alloys.

[1]"Impact Resistance of Some Steels and Welds at Sub-Zero Temperatures", R. K. Hopkins, Director of Metallurgical Research, M. W. Kellogg Company. American Welding Society, Fall Meeting, 1934.

"Mechanical and Non-Destructive Testing of Vessels and Welds with Particular References to Sub-Zero Operation." Paper before British Iron and Steel Institute, May, 1935.

[2]"Nickel Steels at Low Temperatures"—An "Investigation of the Impact Properties of the 2¼% Steels," B. G. Aldridge and G. C. Shepherd, Jr. Metals & Alloys, Vol. 7, No. 6, 147-152; Vol. 7, No. 7, 185-192. (These papers present a comprehensive study of impact testing with relation to location of the specimen in the plate).

[3]"Progress in Metals—Sub-Zero Steels for Propane Dewaxing," W. L. Nelson. Oil & Gas Journal, No. 35, Jan. 14, 1937, page 58.

*An alloy of approximately 2/3 nickel and 1/3 copper. Table II gives a typical analysis.

†Ni-Resist is an austenitic cast iron of the composition: Total carbon 2.75-3.10; silicon 1.00-2.00; nickel 13.00-15.00; copper 5.00-7.00; chromium 1.25-4.00; manganese 1.00-1.50. It is non-magnetic and may be identified by this property.

SULPHURIC ACID

Sulphuric acid is probably one of the earliest reagents associated with refining of petroleum products. The handling of this material has always offered serious corrosion problems. Monel is outstanding among wrought materials in its resistance to sulphuric in concentrations below 95 percent. The resistance of Monel when compared with that of other resistant materials is shown in Figure 1. The high resistance of "Causul Metal" shown is typical of that to be expected from Ni-Resist† cast iron and explains the increasing use of lines of this alloy to convey acid sludges. Valves of "Causul Metal" have been reported as giving a life in excess of nine years in acid sludge service.

The effect of temperature is to markedly increase the corrosive power of sulphuric acid, as may be seen from Figure 2.

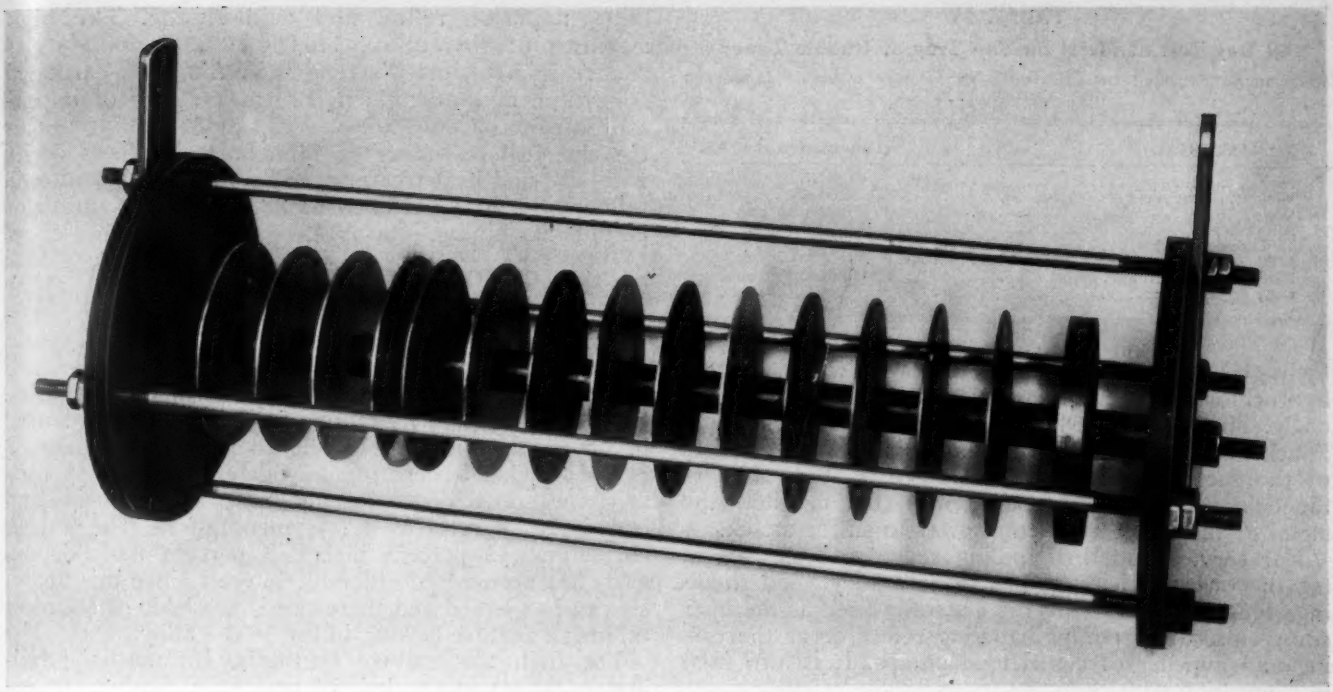
In recent developments in refining there has appeared interest in Monel at temperatures higher than 203° F., the maximum formerly given in Figure 2, therefore, further work was carried out and a point at 220° F. in 60 percent acid determined; this point is shown in Figure 2 and represents a test of 14 days duration under the conditions described. Apparently, lead is the most resistant of commercial metals to sulphuric acid under concentrations of 70 percent over a temperature range of room to 230° F. (the limit explored) but its softness and tendency to creep, which becomes more

TABLE II

Results of Some Low Temperature Tests of Monel Metal

C 0.14	Mn 1.07	Fe 1.30	S 0.005	Si 0.06		Cu 29.66	Ni 67.74
Heat Treatment	Condition of Sample	Yield Point, Lbs./Sq. In.	Maximum Strength, Lbs./Sq. In.	Percent Elong. in 2"	Percent Red. of Area	Ft. Lbs. Izod Impact	Charpy—Ft. Lbs. Std. "V" Notch—0.01" Rad. at Bottom
Forged	As received; tested at room temperature	68,000	92,000	32.0	73.7	119	216
Forged	Held one-half hr. at (−)183° C. −(297.4° F.)	91,500	128,250	44.5	71.8	119	216
Forged	Held 72 hrs. at (−)183° C. −(297.4° F.)	92,500	130,000	43.0	72.7	119	...
Forged	Same but tested at room temperature	.....	.....	....	....	119	...
Heated at 1,750°–1,800° F., for 20 minutes and air cooled	As received; tested at room temperature	29,000	79,000	46.0	77.1	100	189
Heated at 1,750°–1,800° F., for 20 minutes and air cooled	Held one-half hr. at (−)183° C. −(297.4° F.) and tested	49,500	115,250	49.5	73.9	119	184
Heated at 1,750°–1,800° F., for 20 minutes and air cooled	Held 72 hrs. at (−)183° C. −(297.4° F.) and tested	51,250	113,000	47.5	74.1	120	...
Heated at 1,750°–1,800° F., for 20 minutes and air cooled	Held 72 hrs. at (−)183° C. and tested at room temperature	.....	.....	....	....	102	...

NOTE—Data supplied through courtesy Union Carbide & Carbon Corporation Research Laboratory, Niagara Falls, N. Y.



New type specimen holder used in testing corrosion of metals.

pronounced with temperature, limits its usefulness. The highly alloyed materials as the Hastelloy group, especially "D"; the La Bour group, "Illium" and similar alloys high in nickel and containing many other elements are most useful as valve parts and trim, pump parts, especially valves and as protective lining or members to carry loads in reaction vessels.

A reciprocating pump to handle hot acid sludge in quantities should give satisfactory service when containing the parts shown in Table III.

TABLE III

Parts of Reciprocating Pump to Handle Hot Acid Sludge

Liners	—	Cast S Monel (1)
Rings	—	Monel (2) in spring temper
Piston	—	Monel—cast or wrought
Rod	—	K Monel (3) full hardness
Valves	—	High Nickel Alloys (4) as Hastelloy D, La Bour R-55, Illium or similar alloys

(1) Approx. 67 percent nickel; 29 percent copper; 3.75 percent silicon; castings only.
(2) Approx. 68 percent nickel; 29 percent copper; cast or wrought.
(3) Approx. 63 percent nickel; 30 percent copper; 3.50 percent aluminum—cast or wrought.
4) Usually castings.

HYDROGEN SULPHIDE AND HYDROCHLORIC ACID

The average refiner is acquainted with the corrosiveness of hydrogen sulphide. A number of crudes also contain salts that crack to form hydrochloric acid in condensing equipment. At temperatures above the condensing point of water, resistance to hydrogen sulphide is obtained by the use of chromium as an alloying element; within this temperature range hydrochloric gas is not appreciably corrosive. The high chromium alloys containing 18-28 percent chromium have their physical properties improved by additions of nickel and their corrosion resistant properties are also enhanced by this addition. The 18 percent chromium 8 percent nickel alloys are probably the best known of the chrome-nickel corrosion-resisting alloys. Heating-coil tubes of this material have given excellent accounts of themselves from the standpoint of resisting attack by sulphur-bearing gases and oils. The tendency of these tubes to rupture widely when overheated has restricted their use but when intelligently used with a clean and refractory feed stock, tubes of 18-8 are satisfactory. Exchanger tubes of 18-8 can and have given excellent service. The design of the exchanger using these tubes must be such as to readily accommodate the relatively high coefficient of thermal expansion of the alloy.

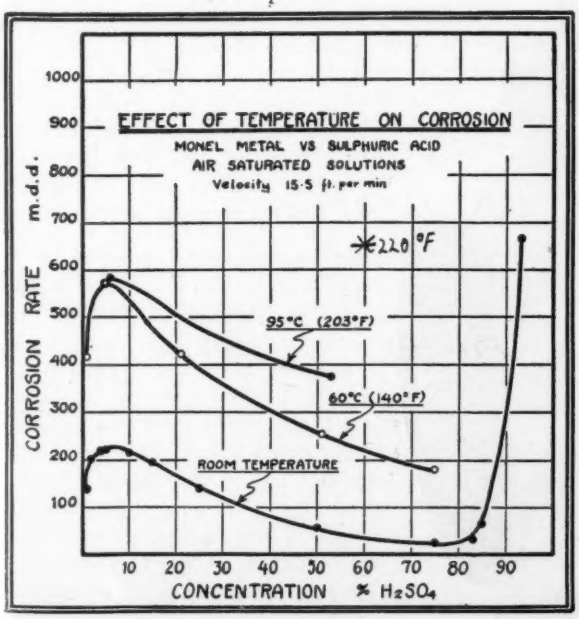


FIGURE 2

Note: to convert to Ins./year multiply by 0.000164.

The 18-8 alloys are widely used as trim for valves in hot-oil lines, as protecting liners in cracking vessels and as baffle plates in heat exchangers. Cast 18-8 headers and return bends are finding wider acceptance for use in heating coils. The working parts of hot oil pumps make generous use of 18-8. Tubes, valves and parts of this alloy are used in connection with solvents containing phenols.

At temperatures where water exists, the attack from

TABLE IV

60 Day Test of Metal on Top Tray of Bubble Tower

Michigan Crude being run. Estimated temperature of liquid in contact with specimen 200°F.

MATERIAL	Penetration Ins./Yr.
Monel	0.0075
Nickel	0.0069
Yellow Brass	0.0240
Admiralty	0.0219
18 Chrome 8 nickel	0.0254
Mild Steel	0.0500
Ni-Resist (Cast Iron)	0.0131 (90 days)
Gray Cast Iron	0.0430 (90 days)

hydrogen sulphide is more like that of a weak acid and hydrochloric acid, when present, attacks metals vigorously. The top part of bubble towers is a location where attack of this nature readily takes place, for regardless of the fact that the top temperature is above 400° F. the cold reflux remains sufficiently cool to allow the metal of the top third of the tower to suffer attack.

For service both in handling reflux and as caps in top of towers, Ni-Resist has made a very good showing. This alloyed cast iron is generally used as the liner for reciprocating pumps handling reflux or as the casing and impeller of centrifugal pumps. It is also used in connection with compressors to handle refinery gases, especially as liners.

Monel possesses a resistance to these condensed acids superior to Ni-Resist. It finds application as orifice plates in sour refinery gases and owing to the retention of diameter of opening and sharp edge, is popular for this service. It is used as a protective liner for parts of towers and lines handling overhead material that is quite corrosive as the result of the presence of hydrochloric acid, hydrogen sulphide and organic acids. Table IV presents data collected during a cooperative test with a leading refiner of Michigan crudes which are often high in chloride salts.

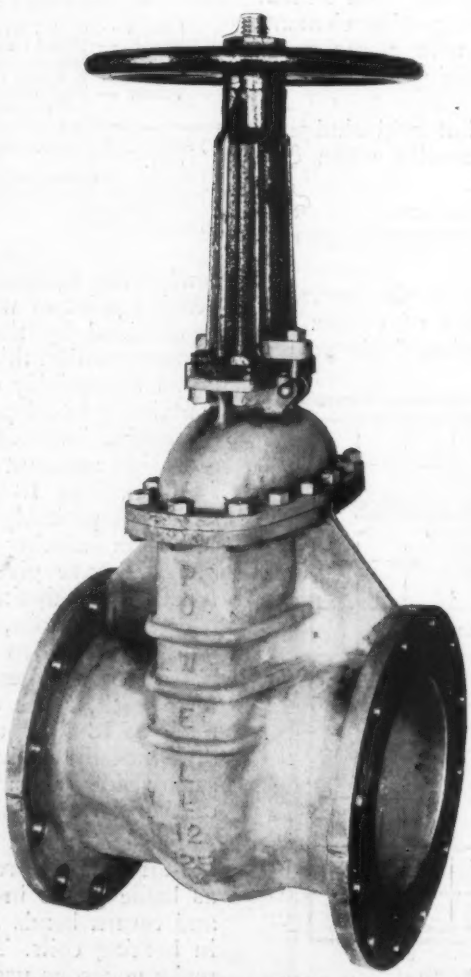
The high order of corrosion resistance of Monel as shown in Table IV is further borne out by the behavior reported for Monel pump valves of the "Durabla" type when handling gasoline or naphtha containing hydrochloric acid and hydrogen sulphide in solution.

K Monel (an aluminum bearing form of Monel) by virtue of the fact that it can be hardened by heat treatment is finding increased use as a pump rod or shaft material for pumps handling naphtha, reflux and acid sludge. The high strength of this alloy, 140,000-160,000 pounds per square inch ultimate strength in the semi-hardened condition, recommends it for valve stems of important steam or cold oil valves. K Monel possesses the chemical resistance of Monel. Its hardness varies with size and heat treatment. The widest application in refineries is in a hardness of 280-300 BHN since this permits machining.

CHLORINE AND ORGANIC ACIDS

Using petroleum and its derivation as a base, refiners are developing side lines of chemicals. As a result, chlorination of paraffins and production of organic acids and chemicals is a familiar feature in many refineries. Equipment of pure nickel or of nickel-clad steel is used in the chlorination work. The 18 percent chromium 8 percent nickel 3 percent molybdenum alloys are used in connection with the production of organic acids and chemicals. A recent development of a 16 percent chromium, 13 percent nickel, 3 percent molybdenum alloy has aroused considerable interest since this analysis can be pierced and therefore is available as seamless tubing; a feature lacking in the 18-8-3 alloy.

For high temperature synthesis, Inconel (approximately 80 percent nickel, 14 percent chromium, 6 percent iron) tubing is finding application. This alloy possesses high chemical resistance to many materials and high resistance to oxidation. It is probably best known as a heat resistant alloy.



A 12-inch gate valve of all Monel construction for use in handling sludge acid at an important petroleum refinery. Main body casting produced at INCO, Bayonne foundry.

TESTING

The wide use made in refineries of the corrosion test rack shown in Figure 3 (furnished by the Development & Research Division, International Nickel Company, Inc.) which has been described and discussed by Messrs. Searle and LaQue[4], shows the refinery metallurgists are keenly aware of their responsibility to keep abreast of their colleagues in the development of better products and a realization that each problem in corrosion must be made the subject of a special study. It is through such cooperative studies that the metal industries are made aware of the problems confronting the refinery metallurgist and are able to cooperate in finding a solution.

[4]"Corrosion Testing Methods," H. E. Searle and F. L. LaQue. Proc. A.S.T.M. 1935, Vol. 35, Part II, 249-260. Reprinted—Bulletin T-10, International Nickel Company, Inc.

Corrosion-Resistant Metals . . .

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FOR many years metal corrosion has been recognized as a major problem of world-wide importance. This is not only on account of the great wastage involved, but also because of the limited services for several commercial metals, particularly iron and steel, that otherwise have a wide range of desirable physical properties.

Interest in this subject is illustrated by the avalanche of symposiums that were held in 1936, which include:

American Society for Testing Materials, on High-Strength Constructional Metals, Pittsburgh, Pa., March, 1936.

Chemical Engineering Congress of the World Power Conference, London, England, June, 1936.

American Chemical Society, on New Metals and Alloys, Pittsburgh, Pa., September, 1936.

American Society of Civil Engineers, on Steel and Light-Weight Alloys, Pittsburgh, Pa., October, 1936.

The American Society of Mechanical Engineers, on Corrosion-Resistant Metals in Design of Machinery and Equipment, New York, N. Y., December, 1936.

The tonnage of steel produced is about eighteen times that of all other metals so we shall refer to that metal in particular in discussing this problem. It has been estimated[1] that nearly one billion tons of steel are in use today in this country. The annual cost of maintenance, protection, and partial replacement of such a large quantity of metal is certainly a substantial figure, even without reference to consequential losses, and regardless of whether it is estimated at thirty cents or one dollar per ton, and the latter figure is probably a closer estimate. This rather conservative appraisal of the annual losses due to corrosion serves to illustrate the economic importance of the problem.

Several of the nonferrous metals play an important part in widening the application of steel, either by alloying, or plating, or in some instances by veneering, to obtain better resistance under certain conditions of exposure.

The production of low-cost higher-strength steels in lighter sections for transportation reconstruction and other structural purposes necessitated reduction in the corrosion rate. Fortunately, this was accomplished, in the case of metals subject to atmospheric corrosion, by the proper blending of small amounts of alloying elements such as chromium, copper, nickel, silicon, or phosphorus in steel.

At least one of these low-alloy higher-tensile steels shows two or three times the resistance to attack in water compared with carbon steel. This is encouraging in view of the fact, demonstrated by many extensive tests during the past 25 years, that no material difference was found in the rate of corrosion between any of the well-known commercial types of ferrous metals when used in water or in soils. In corrosive soils, where local electrolytic conditions predominate, the metal-corrosion problem is much more difficult, and at present it is necessary to resort to protective coatings or cathodic protection by counter electric current impressed on the metal.

About a decade ago the number of metals available for use in the chemical industry was comparatively limited. New developments in chemical processes on a large scale created a demand for new metals or alloys suitable for high and low temperatures and resistant to many types of severe corrosion and scaling. Such metals usually have to be capable of being forged, cast, or welded with facility. Many new metals and alloys, ferrous and nonferrous, have been developed recently for such service as well as for bearings, antigalling joints, and many other purposes, and these have been responsible in a large measure for the remarkable progress in certain industries during recent years. For example, consider the application of modern alloy steels in the production and refining of petroleum and what improving the quality and lowering the cost of petroleum products have done for other industries.[2]

Two groups of factors are involved in corrosion; those associated with the metal and those associated with the environment. The essential points of the process or mechanism of corrosion of metals may be explained by the following facts:

The common metals (for example, iron, nickel, chromium, and copper) are relatively unstable with respect to their environment. They have been won from their ores by expenditure of considerable energy and attempt to revert

with a decrease in free energy of the system to the more stable combinations (oxides, carbonates, etc.) in which form they are found in nature.

The mechanism of corrosion involves the surface chemistry of metals. The reaction of the metal with its environment may be by direct chemical union, as in the case of oxidation or scaling at elevated temperatures, or by more complicated reactions when the metal is in contact with an electrolyte, such as water, or an aqueous solution.

Considering the most common types of corrosion of metals, which occur only in the presence of liquid water, essentially there are two main steps in this interaction. The first is the initial tendency of the metal to enter solution. The driving force is referred to as the solution pressure of the corroding metal or the potential between adjacent parts of the metal surface. The initial corrosion is also governed by the metal composition and its structural homogeneity, surface finish, inherent power to form surface films, local strain, and overvoltage of hydrogen deposited on the metal. The second may include several reactions that determine the rate of deterioration and, therefore, the useful life of the metal.

In the case of iron and many of the commonly used metals, the initial rate of solution is likely to be quite rapid, and, if this is not opposed, the life of these metals in such cases would be relatively very short. Fortunately, this tendency of metals to dissolve in water is resisted by natural layers or barriers of corrosion products (solid, liquid, or gaseous) that retard and sometimes stop the reaction before any material damage is done. These protective layers consist mainly of films (sometimes invisible) or thicker corrosion deposits.

A number of factors having to do with the secondary reactions play an important part in the building up or breaking down of these metal surface layers. The principal ones are: (1) acidity; (2) free oxygen; (3) flow velocity; (4) temperature; (5) cyclic stress; (6) materials in the metal or environment that assist in forming the protective layer; and (7) various contact effects.

Some of these factors affect the average rate of attack and others the distribution of corrosion, and all are likely to have an important influence on the life of the metal. Localized attack is, of course, important in the case of pipe or containers, as pitting may cause perforation of the metal long before it has lost much in weight.

In the presence of water, corrosion is accompanied and promoted by electrochemical reactions. That is, the metal enters the solution at certain anodic areas and an equivalent amount of hydrogen is plated out at adjacent cathodic areas. The anodic and cathodic reactions occur simultaneously. Free oxygen or oxidizing compounds accelerate attack on the metal by combining with the polarizing film of hydrogen. If oxygen is not available for this purpose, corrosion is reduced to a negligible amount in water that is alkaline or only slightly acid, but if the acidity is sufficient to cause evolution of gaseous hydrogen, the way is open for more metal to dissolve. If the anodic and cathodic areas are relatively small, corrosion will be fairly uniformly distributed. On the other hand, the attack becomes more localized in the form of pits as the ratio of anodic to cathodic areas is reduced and as the electrical conductivity of water increases. It follows that attack on the metal would be more uniformly distributed when the ratio of anodic to cathodic area is increased, and the electrical conductivity of the solution is decreased.

Pitting is promoted by any local increase in potential. This is due mainly to contact with dissimilar metals or other material on the surface, such as mill scale on steel, concentration or solution cells, or internal strain. Differences in oxygen concentration in water solution have proved to be the most common cause of pitting, the area exposed to the solution that is highest in oxygen being cathodic to parts exposed to lower oxygen concentration. In other words, corrosion occurs more rapidly where the solution next to the metal is deficient in oxygen. Deposits of corrosion products, cracks or angles in the structure, or solid foreign matter of almost any kind that interferes with diffusion are likely to result in variations in oxygen concentration sufficient to form an active concentration cell at such spots on the metal. Variations in concentration of solutions or solutions of different materials set up solution cells with the same result. It is, therefore, important in designing structures subject to corrosion to keep the metal surface as clean as possible. Dust particles in the air, especially when a little sulphur dioxide is also present, accelerate electrolytic action when the relative humidity is in excess of 70 percent.

Variable stresses far below the fatigue limit in air, when accompnaied by water corrosion, may cause early failure. The endurance limit of carbon or alloy steels has been reduced from half the tensile strength to as low as 12,000 pounds per square inch under such conditions. Special precautions should be taken to protect parts from corrosion when under high cyclic stresses.

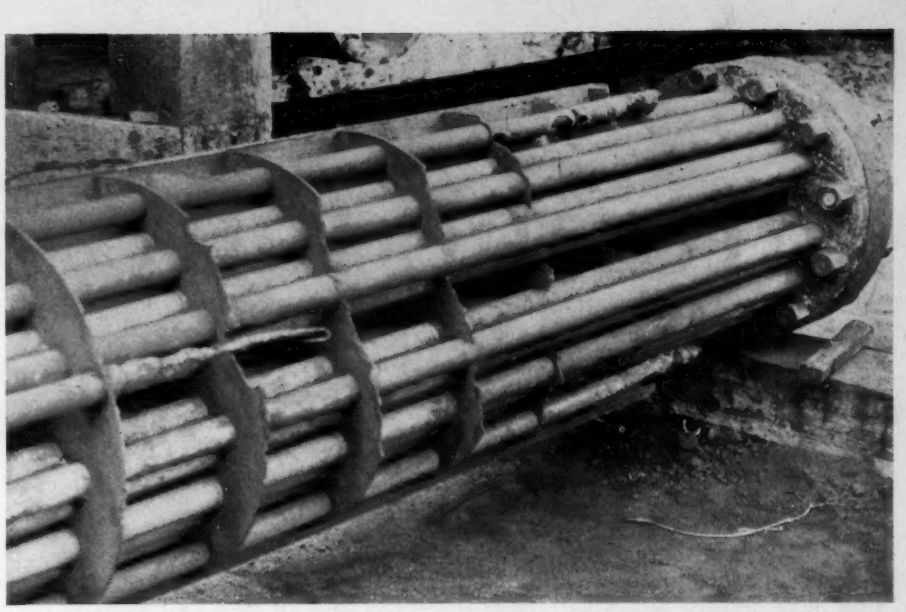
Sometimes the attack is directed along grain boundaries or other lines of weakness in the metal, as in dezincification of brass, graphitization of cast iron, or the grain-boundary attack sometimes found in unstabilized 18-8 chromium-nickel steel.

The factors referred to and many others rarely act independently; the effect of each is modified by others. For example, velocity of flow increases oxygen depolarization on iron up to a certain point above which it promotes the building up of ferric protective films and corrosion decreases. However, one or two factors usually control the rate of corrosion.[3]

The rate of corrosion may be considered as analogous to flow of water under pressure in a pipe line in which there are several different valves. The flow may, of course, be controlled by partly closing one or more of these valves. For example, corrosion is sometimes encountered in gasoline pipe lines, especially near the inlet. Water and oxygen are slightly soluble in gasoline. The water condenses out on the inside wall of the pipe when the gasoline is cooled, for instance, by contact of the pipe with the ground. Plenty of free oxygen is available in the gasoline to keep the reactions going. In this case corrosion may be brought under control by dehydrating the gasoline, removing the free oxygen, or by injecting a soluble inhibitor that will be taken up by the condensed water and build up a protective film. However, only one of these

expedients need be used to prevent the metal from being seriously damaged.

The corrosion problem is now recognized not as a single one, but rather as a group of problems complicated by many variables, the result of which determines the rate of attack. Corrosion types may be classified in various ways, but it seems logical to group them according to the common controlling factors. In view of the fact that factors external to the metal usually predominate, it is convenient, to classify corrosion according to the environment, and thus we may speak of it as atmospheric, underwater, soil, chemical corrosion, or electrolysis due solely to stray electric currents. In atmospheric corrosion the predominant factor is moisture; in water, oxygen concentration; in soil, electrical conductivity, total acidity, and water content. This system of classification is useful in corrosion testing and in considering the most economical means of prevention.



Alloy steel tubes are not corroded in this exchanger bundle, but the iron support members has been seriously affected. Exchanger in refinery oil-to-oil service.

Most preventive measures[4] may be divided into three groups according to the principle employed: (1) Paints, lacquers, and other applied coatings; (2) treatment of environment to make it less active toward metals (for example, by the addition of soluble alkalies, chromates, phosphates, or silicates to water to assist in forming a natural protective layer on the metal); and (3) the use of metals that have the power to form self-healing protective films with the particular environment under consideration. As the purpose of the two latter principles is to build a resistant film by reaction between the metal and the environment, it is obviously necessary to make a thorough analysis of all the surrounding factors before attempting to select or develop a metal that will react favorably and protect itself for a reasonable time. It is important to remember that in corrosion problems we are dealing not with the real metal surface but with metal-surface films. Natural protective layers are more easily formed in air than in solutions or in soils. For instance, the addition of 0.20 percent copper will double the resistance of steel in industrial air at an increase in cost of about $3 per ton, but copper steel shows practically no advantage when submerged in domestic or sea water.

Where chemical solutions are involved each case is usually a separate problem and no metal has been found that is proof against all conditions without the aid of some additional protective coating. For example, in certain soils the local electrolytic action of moist soil particles sets up such a strong differenece of potential that it sometimes breaks down the protective film on copper, 18-8 chromium-nickel steel, or 27 percent chromium steel. There are exceptional cases, but as a rule the difference between all the common types of ferrous metals, including copper steel and 5 percent chromium steel, is not material in soils, as shown in the Bureau of Standards' exposure tests.[5]

Summary

It does not seem likely that we shall find one metal or one general remedy for all kinds of corrosion. The metal and environment must be mated so as to live together peaceably, at least until the owner gets a reasonable return on his investment. This is essentially an economic problem, the answer to which may be to let the structure alone and recondition when necessary, as is often the practice in buried pipe lines; to apply a coating of a more resistant material; to condition the environment so that it will be less active; or to select the metal or alloy best adapted to the particular conditions of service at the lowest consistent cost. Structural design, regulation of environment, and care of metals are important factors in their life. It should be remembered that metals are, in a way, quite like human beings; although they are susceptible to unfavorable environment, their resistance can be built up by inoculating them with alloying elements and by keeping their surfaces reasonably clean and free from foreign deposits. As the useful life of any metal is determined mainly by the film-building properties of both the environment and the metal, and as metals have to live under so many conditions of service, it is extremely improbable that any one metal can be made at reasonable cost that will meet all the common conditions of service. The problem of the engineer, therefore, is to select the metal that will best serve any specific purpose at the lowest ultimate cost. Too much attention may be given to first cost.

REFERENCES

* Introductory paper to a symposium on Corrosion-Resistant Metals, in the Design of Machinery and Equipment held by the Iron and Steel Division and presented at the annual meeting, New York, N. Y., of The American Society of Mechanical Engineers. Republished here through the courtesy of the society and its journal, *Mechanical Engineering*.

[1] American Iron and Steel Institute, *Iron Age*, vol. 137, April 2, 1936, p. 71.

[2] See papers and discussions on this subject presented at the symposium of American Chemical Society, and published in *Industrial and Engineering Chemistry*, December, 1936.

[3] Those interested in details of these corrosive reactions may refer to "The Corrosion of Metals," by Ulick R. Evans, Arnold and Co., London, 1926; "Corrosion Resistance of Metals and Alloys," by McKay and Worthington, Reinhold Publishing Corp., New York, N. Y., 1936; "Corrosion—Causes and Prevention," by F. N. Speller, McGraw-Hill Book Co., New York, N. Y., 1936.

[4] "Influence of Protective Layers on the Life of Metals," by F. N. Speller, MECHANICAL ENGINEERING, vol. 57, no. 5, 1935, pp. 355-360.

[5] U. S. Bureau of Standards Research Paper No. 883, May, 1936.

CROLOY 2 AND CROLOY 3-M

Intermediate Steels for Refinery Service

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The Babcock & Wilcox Tube Company

IN THE past three years several low alloy content steels having properties suitable for refinery application have become available. These steels fall into an intermediate position both as to alloy content and cost between plain carbon steel and the well known 5 percent chromium, 0.50 percent molybdenum alloy steel which has been used to advantage for some years in the refining industry. It is of interest at this time to trace the development of steel of the intermediate type and to cite the properties and characteristics of this and one other steel falling into this intermediate classification. The present discussion is directed mainly to seamless tubing application inasmuch as much of the tonnage has been in this form for use as still tubes in various types of cracking furnaces.

SELECTION OF ANALYSIS

The handling of large volumes of sweet or mildly corrosive oil following the discovery of East Texas, suggested that there was a place in the refinery for a low alloyed steel of nominal cost with corrosion resistance substantially better than plain steel. In addition, because pressure conditions were, in general, increasing, it was felt that the high-temperature strength properties of the intermediate alloy should be equal or better than the 5 percent chromium-molybdenum type.

Accordingly, the metallurgical department of the writer's company gave consideration to several steels that might be suitable for the purpose and selected an analysis range for the new steel. This composition range, together with the range for an additional steel developed later, known as Croloy 2 and Croloy 3-M respectively, is as follows:

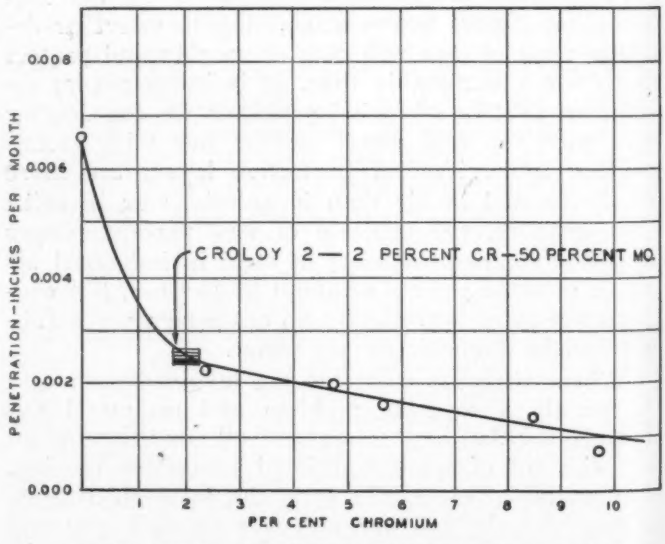
TABLE 1
Chemical Specification

	Croloy 2*	Croloy 3-M*
Carbon	0.15 Max.	0.15 Max.
Manganese	0.30—0.60	0.30—0.60
Sulphur	0.030 Max.	0.030 Max.
Phosphorus	0.030 Max.	0.030 Max.
Silicon	0.50 Max.	0.50 Max.
Chromium	1.75—2.25	2.75—3.25
Molybdenum	0.40—0.60	0.80—1.00

* These steels now appear as Grades 4 and 5 in Manufacturers' Standard Specifications No. 202-36 "Seamless Intermediate Alloy Steel Still Tubes for Refinery Service."

The chromium range for Croloy 2, commonly known as 2 percent chromium, 0.50 percent molybdenum steel, was chosen after a careful survey of refinery corrosion data on steels of various chromium contents. Particular attention was paid to Mr. E. S. Dixon's curve[1] on corrosion rate versus chromium content which is reproduced in Figure 1. The chromium range of Croloy 2 is indicated on this curve wherein it may be noted that the chromium range chosen is exactly on the "knee" of the curve which results in maximum corrosion resistance for minimum cost. Beyond 2.25 percent chomium, the upper limit of chromium for Croloy 2, the curve becomes appreciably flatter and further small increases in chromium content result in relatively little improvement in resistance toward corrosion.

The usual addition of molybdenum, i.e., 0.40 to 0.60 percent, was added to assist creep strength properties and for the further effect of reducing temper-brittleness evidenced by many of the plain chromium-containing steels. Silicon, in both Croloy 2 and Croloy 3-M, was held to 0.50 percent maximum due to the feeling that increase of silicon content to a point where it would materially assist oxidation resistance would tend to detract somewhat from high-temperature strength properties. Steels of the type under discussion are pro-



RELATION BETWEEN CORROSION RATE AND CHROMIUM CONTENT WHEN HANDLING CERTAIN CORROSIVE CRUDES AT HIGH TEMPERATURE AND PRESSURE, (AFTER DIXON) — CROLOY 2 SUPERIMPOSED ON CURVE.

FIGURE. 1

duced by the electric furnace process and thus high quality material is assured.

Tubing, as annealed, of either alloy will consistently meet the minimum physical requirements given in Manufacturers' Standard Specification No. 202-36. These minimum requirements are as follows:

Tensile Strength, lbs. per sq. in.	60,000
Yield Point, lbs. per sq. in.	25,000
Elongation in 2 inches, percent	30
Brinell hardness, maximum	163

The Croloy 3-M composition was selected some time after the introduction of Croloy 2 to provide even greater strength properties than Croloy 2, additional chromium being added to provide some margin of improvement in both resistance to corrosion and oxidation. Strength increase at elevated temperature was secured by increasing the molybdenum to 0.80 percent to 1.00 percent, an average content of 0.90 percent being the value aimed for in production material.

PHYSICAL PROPERTIES AND CHARCTERISTICS

Tubing for refinery use is practically always used in the annealed condition so that operations of rolling, expanding, bending and forming can be performed without undue difficulty. Typical physical properties of Croloy 2 and Croloy 3-M, annealed, at room and elevated temperature, are given in Table 2.

TABLE 2
Room Temperature and Short-Time Elevated Temperature Properties
Tests on 1 inch round, annealed.

Temp. °F.	CROLOY 2				CROLOY 3-M			
	Ultimate p.s.i.	Yield* p.s.i.	El. Pct. 2-inch	Red. Percent	Ultimate p.s.i.	Yield* p.s.i.	El. Pct. 2-inch	Red. Percent
Room	66,400	40,050	36.5	63.0	72,250	36,000	34.0	73.3
800	64,300	22,875	26.5	62.5	58,750	33,650	24.5	67.7
900	61,600	22,250	30.5	71.7	53,375	33,200	36.5	76.4
1,000	55,300	21,000	35.0	76.9	45,200	39,800	40.0	82.4
1,100	44,250	20,650	40.0	72.0	35,740	23,150	48.0	88.0
1,200	30,850	19,300	58.0	87.8	24,650	19,675	57.0	93.6
1,300	19,380	17,700	76.5	91.8	18,870	13,620	69.0	96.5

* Yield point from Amsler stress-strain diagrams.

From the values shown in Table 2, it may be noted that Croloy 2 shows somewhat lower tensile strength and higher yield point at room temperature and consistently higher short-time tensile strength than Croloy 3-M. On the other hand, Croloy 3-M shows superior yield strength values at elevated temperature and the significance of this becomes apparent on examination of the comparative creep strength values for these alloy steels.

CREEP PROPERTIES

Creep tests, covering the range 1000° F., 1100° F., and 1200° F., have been made by Professor F. H. Norton, Massachusetts Institute of Technology, under a fellowship maintained jointly by The Babcock & Wilcox Tube Company and The Babcock & Wilcox Company. The tests on Croloy 2 were made on strip specimens cut from mill annealed cracking still tubes while those on Croloy 3-M were from annealed 1-inch round representing a commercial 25-ton electric furnace heat of the alloy. Chemical analysis, McQuaid-Ehn grain size and Brinell hardness of the material tested for creep were as follows:

	Croloy 2	Croloy 3-M
Carbon	.115	.11
Manganese	.40	.45
Sulphur	.015	.012
Phosphorus	.015	.012
Silicon	.40	.33
Chromium	1.91	3.03
Molybdenum	.51	.90
Ehn Grain Size	5-8 (4's)	4 to 6
Brinell	143	143

The McQuaid-Ehn grain size[2], determined by the standard carburizing test, has a considerable bearing on the properties of steel, especially hardening characteristics, resistance to impact at sub-zero temperatures and upon high temperature strength properties. The inherent or McQuaid-Ehn grain size is controlled largely by the melting and deoxidation technique employed in melting the steel, but it may be altered to some extent by mechanical and thermal treatment during or after rolling. Generally speaking, the coarser grain types, having 1 to 4 grain size, are somewhat more resistant to flow at high temperature than the fine-grained type having 5 to 8 grain-size[3]. At times, a compromise is necessary in order to ensure satisfactory impact properties at low temperature. Both Croloy 2 and Croloy 3-M have satisfactory impact properties at or near room temperature but if consistently good impact values are required at —25° F., the fine grain types must be used.

The steels tested for creep had an intermediate grain-size in the case of the Croloy 3-M, and a fine grain in the Croloy 2. The creep tests conducted by Professor Norton on these steels were made in accordance with the tentative code[4] for such tests. Specimens were 36 inches overall length and of 10-inch gauge length. The tests were conducted using single-step loading and tests

TABLE 3
Creep Stress Data[a]

RATE	1,000°	1,100°	1,200°
CROLOY 2			
.01 percent 1,000 hours	6,300	3,325	1,075
.10 percent hours	11,000	5,875	3,400
CROLOY 3-M			
.01 percent 1,000 hours	7,000	4,200	*
.10 percent 1,000 hours	10,500	9,000	4,000
CROLOY 5-M (5 Percent Cr.—0.50 Percent Mo.)			
.01 percent 1,000 hours	7,200	2,400	900
.10 percent 1,000 hours	9,200	4,800	1,800

a Values in pounds per square inch.
* Stress for .01 percent 1,000 hours at this temperature not certain yet as tests are still in progress.

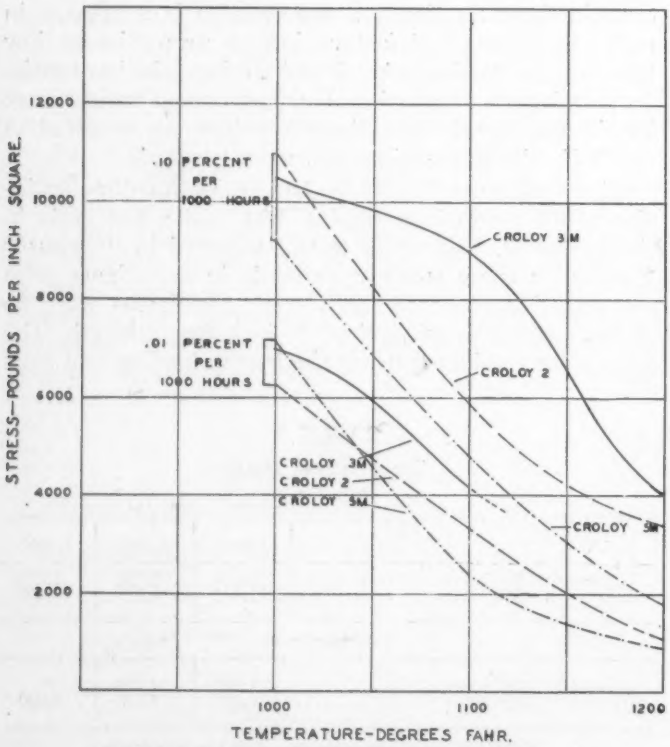
ranged from a minimum time under load of 1000 hours to as long as 6000 hours. Average testing time for the Croloy 2 specimens was 2520 hours and 2416 hours for the Croloy 3-M or somewhat over 90 days each. The creep stress values for creep rates of .01 percent and .10 percent per 1000 hours obtained in these tests are given in Figure 2, which shows the strength properties of these steels in comparison with 5 percent chromium, 0.50 percent molybdenum alloy. It may be noted herein that Croloy 2 shows superior resistance to creep over 5 percent chromium, 0.50 percent molybdenum steel with Croloy 3-M considerably superior to either at temperatures in excess of 1000° F. Stress values for these rates of creep are also given in Table III.

THERMAL EXPANSION DATA

Values for the linear coefficient of expansion have been determined for both steels, the average mean coefficient of several determinations for each alloy being as follows:

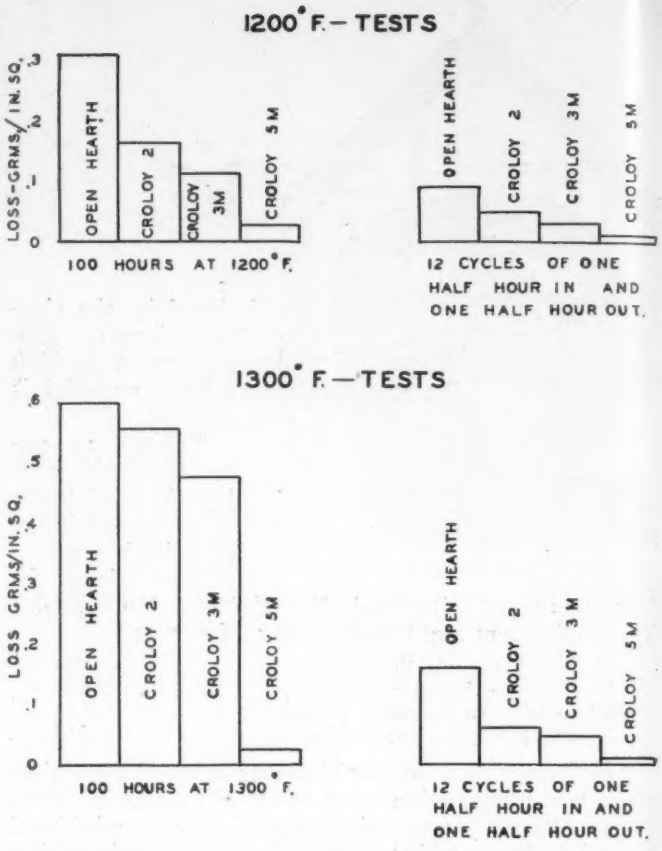
	Degree F. Temp. Range.	Mean Coefficient Inches per Inch per ° F.
Croloy 2	70° to 450°	7.45 x 10–6
	70° to 750°	7.78 x 10–6
	70° to 1050°	8.45 x 10–6
	70° to 1150	8.50 x 10–6
Croloy 3-M	70° to 410	7.51 x 10–6
	70° to 802	7.75 x 10–6
	70° to 1005	7.81 x 10–6
	70° to 1209	8.06 x 10–6

The linear expansion coefficients of these alloy steels are quite similar to carbon and carbon-molybdenum steel and are but slightly higher than 5 percent chromium, 0.50 percent molybdenum steel so that such materials can be used in conjunction with each other



CURVES SHOWING COMPARATIVE CREEP STRENGTH OF CROLOY 2, 3M&5M FOR RATES OF .10 & .01 PERCENT PER 1000 HOURS (AFTER NORTON).

FIGURE 2



COMPARATIVE OXIDATION RESISTANCE AS DETERMINED BY CONTINUED HEATING, AND CYCLIC TESTS (ALTERNATE HEATING AND COOLING).

FIGURE 3

in the same assembly without encountering trouble due to differences in expansion rate.

OXIDATION RESISTANCE

The intermediate alloys are not as resistant to oxidation as the 5 percent chromium alloys, nevertheless, they are appreciably better than the carbon steels. In this respect, Croloy 3-M is somewhat superior to Croloy 2, as may be noted from both long heating and cyclic heating, i.e., alternate heating and cooling in an oxidizing atmosphere at 1200° F. and 13° F. Comparison with carbon steel and 5 percent chromium, 0.50 percent molybdenum steel (Croloy 5-M) is given in Figure 3. The superiority of Croloy 5-M (5 percent chromium, 0.50 percent molybdenum) alloy becomes more apparent at 1300° F., which is above the usual service temperature for steels of the intermediate type. The tests were made on samples of uniform size heated in an electric muffle furnace.

MICROSTRUCTURE

Both Croloy 2 and Croloy 3-M are steels of the pearlitic type and, in the annealed state, have structures consisting of ferrite and pearlite. Croloy 2 has a tendency toward spheroidization of the carbides while Croloy 3-M, being of higher alloy content, is even more inclined toward spheroidization; consequently the pearlite is in a completely spheroidized form. Structures, at low and

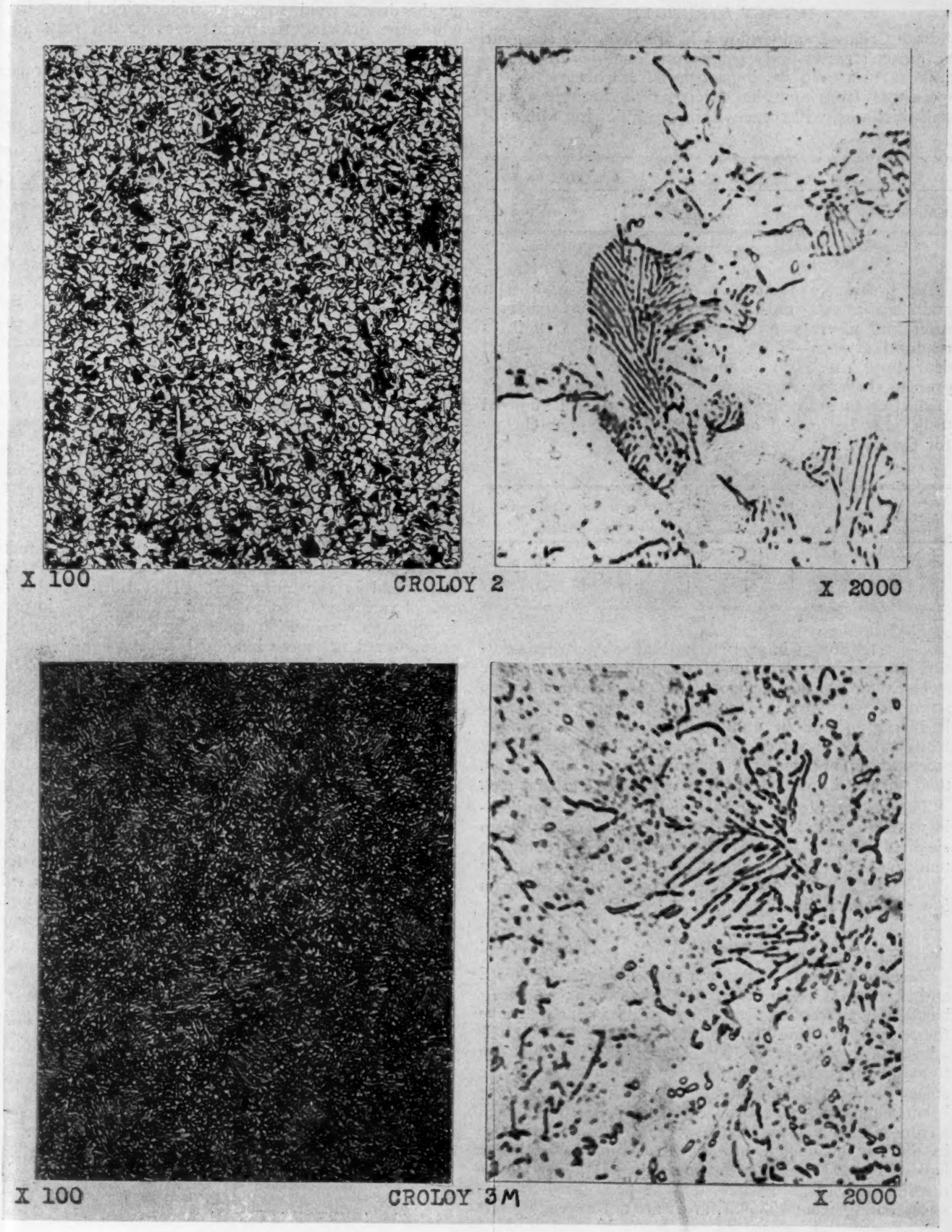


FIGURE 4

Typical structures of Croloy 2 and 3 M from mill annealed cracking still tubes. Etchant: Nital.

high magnification, of commercially annealed tubing are illustrated in Figure 4.

IMPACT STRENGTH

Both Croloy 2 and Croloy 3-M are favorably resistant to impact stresses and exhibit good qualities of toughness as measured by impact tests. Impact values of specimens from annealed tubing, representing various wall thickness, will come within the following range:

	Impact Value, Ft. Lbs.
Croloy 2	55.0 to 80.0
Croloy 3-M	45.0 to 70.0

* Charpy Test—.394 inches square specimens, drilled key-hole notch.

As previously related, inherent or McQuaid-Ehn grain size affects impact strength at sub-zero temperatures and where consistently good impact strength is required at say —25° F., it is necessary to use steel deoxidized in such manner as to produce fine grained characteristics. Relationship of impact strength (Charpy) to grain-size established by several hundred tests, may be quoted in the typical tests given below for Croloy 2:

McQuaid-Ehn Grain Size	Impact, Ft. Lbs. Room Temperature	Impact, Ft. Lbs. Plus 25° F.	Impact, Ft. Lbs. Minus 25° F.
2-5	65, 59	52, 51	10
2-5	60, 69	58, 41	5, 7
6-8	72, 62	77, 62	53, 57
6-8	54, 64	65, 57	46, 47

The retention of impact strength at sub-zero temperature is relatively less important in high temperature steels than is the development of maximum creep strength properties which connotes steels of more or less coarse inherent and actual grain size. Cleaning while tubes are warm will eliminate breakage of any steels which, because grain size or chemical composition, tend to lose impact strength at sub-zero temperatures.

These steels also retain their impact strength on heating and after cooling from long periods of exposure to elevated temperature and susceptibility tests[5] show no tendency for the development of temper-brittleness (cold brittleness) such as was encountered in the plain 5 percent chromium steel[6,7].

WELDABILITY

Because of their chromium content, both Croloy 2 and Croloy 3-M are air-hardening steels, i.e., they harden on air cooling from temperatures near or above their transformation temperatures. For this reason, it is advisable to preheat to 300° F., or higher for welding to avoid stress cracking and to anneal following welding so as to avoid the possibility of shock failure of the hardened metal in or near the weld zone, the Brinell hardness of which may range from 275 to 375 or more in the "as welded" condition. Annealing restores the hardened weld metal and affected zone to a state of ductility and toughness and may be performed by furnace cooling from 1575° F. at a rate not exceeding 60° F. per hour or by drawing for a short time at temperatures between 1325-1375° F., and cooling in air. The full annealing treatment completely restores the air hardened weld zones to their original properties while the drawing treatment gives partial restoration adequate for most applications.

The alloys may be welded by the atomic hydrogen, metallic-arc or acetylene methods. The metallic-arc process is generally recommended because of the unavailability of atomic welding equipment while the acetylene process makes for increased difficulty in controlling the carbon content of the weld deposit. Direct current welding is generally more satisfactory than alternating current welding; peening of the weld beads is unnecessary. Metallic electrodes designed to give weld metal equivalent in composition to the alloy being welded, should be used except in those cases where the alloys are to be joined to carbon steel in which case ordinary carbon steel electrodes should be employed. Standard forms of joints are satisfactory and if possible, backing up strips or rings should be used to ensure full penetration to the bottom of the weld Vee.

APPLICATIONS

Croloy 2 has found wide application over the past two years as tubes in cracking furnaces and vapor lines and to some extent in heat-exchanger equipment. Croloy 3-M has found a more limited application where its higher strength properties over Croloy 2 could be used advantageously. Croloy 2 still tubes have been used in the construction of several new units by major refining companies, in combination and ordinary cracking furnaces and in reforming units. The alloy has also replaced carbon steel tubes in radiant banks and in other locations in cracking furnaces where corrosion has been encountered or where bulging has been troublesome in carbon steel tubes due to pressure and temperature conditions.

The characteristics of these alloys of enhanced resistance to oil corrosion and scaling over carbon steel, with elevated temperature strength properties exceeding 5 percent chromium, 0.50 percent molybdenum steel and lastly their nominal cost, place these materials in an important position for refinery application. The increasing use of the so-called intermediate steels show them to have a useful place. The development, specialization and intergradation of refining processes suggests that steels of the type described herein can be used to advantage by refinery engineers and operators for improving yields or quality of product and for lowering maintenance costs on equipment.

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Metallurgical Aspects *of Alloy Steel for* Refinery Equipment

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THE petroleum refining industry in its effort to develop better and higher quality products has devised new processes requiring equipment to withstand much more severe service both from a physical and heat-resisting standpoint than earlier practice. Today the modern refinery has in service all kinds of steel from the plain carbon and low-alloy types to the highly alloyed chromium-nickel stainless and heat-resisting varieties. It is the purpose of this paper to discuss briefly the metallurgical aspect of these products from a manufacturing and use standpoint.

PLAIN CARBON STEELS

The plain low-carbon steels containing about .10 percent carbon are made either open or killed. The open or rimming type is used for general sheet or plate work, such as tanks, shells or similar structure requirement, also in pipe and tubing. The low-carbon type killed with silicon and aluminum is a very sound, uniform product and in some cases used for still tubes. The low-carbon range has a tensile strength of about 55,000 p.s.i. Increasing the carbon to around .20 to .30 percent will raise the tensile to about 75,000 p.s.i. This is used in heavier plates for tank work where higher physicals are required as well as structural jobs.

The carbon steels with low- and medium-carbon content are made in the open hearth furnace of approximately 75 to 100-ton capacity, although they may run higher. The ingot will vary considerably in size from around 4,000 pounds to up around 80,000 pounds for rolling into large and heavy plates. The ingots are heated to about 2250 to 2300° F. and rolled either directly to finished plate or to an intermediate bloom or slab which can be inspected and all defects removed by chipping. These are then reheated to about 2250° F. and rolled to finished product or tube rounds for later piercing. These usually run about 3 to 5½ inches in diameter. They are inspected again and all defects removed by chipping before being sent to the tube mill.

ALLOY STEELS

The simplest of the alloy steels are the comparatively new low-alloy high-tensile steels used chiefly for mobile equipment to reduce weight through use of higher strengths. These products develop their strength from such alloying elements as copper, molybdenum, nickel, chromium, manganese, etc., from small amounts up to 1 or 2 percent. They contain low carbon to reduce air hardening as far as possible; hence, are well adapted to welding and general fabrication. They possess tensile strengths of about 70,000 to 90,000 pounds per square inch with high yield point. They are, therefore, a good structural material. These steels are made in the open-hearth furnace, can be either open or killed, and are cast in ingots and rolled to various shapes similar to the plain carbon steels.

The general alloy steels such as the S.A.E. types 2340, 3140, 4140, etc., are generally used in the heat-treated condition for such applications as bolting or other requirements necessitating a material with high tensile strength along with good ductility and often machinability. These products meet the A. S. T. M. requirements for high-temperature bolting very well. For high-temperature work, the chrome-moly steels are quite satisfactory, as moly along with chrome increases creep strength at high temperatures apparently better than other alloys.

These alloy steels may in some cases offer better corrosion resistance than the carbon steels, but they are not designed for that purpose, being intended solely for their high physical properties.

The nickel steels, especially the 2300 series containing about 3.5 percent nickel, possess good impact strengths at low temperature and are used for such low-temperature apparatus as de-waxing equipment.

The S.A.E. alloy steels are made in either the open hearth or electric furnace, depending upon requirements, although the former is the most widely employed. In either case the steel is killed and cast into ingots of various sizes but averaging around

4,000 to 6,000 pounds and rolled into blooms or billets. Rolling temperatures are generally about 100° F. lower than for the carbon steels. Soaking time and rate of rolling is longer and slower, and particular care is placed on inspection and removal of all surface defects at each conversion. The billets, after conditioning, are rerolled to finished size bar for heat treating to physicals and are cold drawn for accurate size and surface as the case may be.

SEMI-STAINLESS STEELS

Semi-stainless steels contain generally higher chromium content than the S.A.E. alloys, but not as high as the stainless grades. They run from about 2 to 10 percent chromium, the most popular being the 4-6 percent chromium type. These are used mostly in tubular products as still tubes, transfer lines, condenser tubes, etc. Some have been used in sheet form as traps, caps, etc., in bubble tower and related equipment. Such alloys may contain about .50 percent moly to reduce age embrittlement at certain temperatures and increase creep strength, or 1.0 percent tungsten to increase physical strength as well as .50 percent titanium to reduce air hardening. They possess high physical properties and are more corrosion and heat-resisting than the carbon steel at high temperatures, but are not in a class with the stainless alloys. They are to be considered as intermediate alloys between these two groups.

These grades of steel are all made in the electric furnace of either the arc or induction type. The arc furnace is generally of the Heroult type, operating on a three-phase power circuit and with capacities up to about 30 tons is common practice, although larger furnaces have been employed. A common process for making a heat of this steel or of the higher alloyed stainless type would be as follows. Charge a good grade of heavy-melting scrap and melt under an oxidizing slag to refine or reduce ingredients to desired amount. Remove the slag and make up a new lime silica reducing slag. Then add ferro manganese, ferro silicon, ferro chrome or other alloys as may be required to produce the required analysis; test for temperature and when proper pour the steel into a ladle for casting into molds, producing ingots of 4,000 to 5,000 pounds. These alloys are made in various carbon contents and since ferro chrome is the alloy most abundantly added, it will be necessary to use the quite expensive low-carbon type when making low carbon steel. This is especially true with the stainless alloys and materially increases production costs over the higher carbon grades. The chrome is preheated to prevent chilling of the bath and can be added all at once with the 4-6 percent chrome or lower alloys, but is added in several portions when making the stainless alloys.

Of the induction furnace there are two general types in commercial use. The most generally used consists of a crucible surrounded by a copper coil, water-cooled and operating on a high-frequency power circuit. The copper coil acts like the primary of a stepdown transformer, setting up a magnetic field which generates a current in the charge of scrap in the crucible acting as a secondary. The resistance offered by the steel scrap to the current develops sufficient heat to melt the charge. Such furnaces are in service up to 4 tons capacity.

The other type consists of a circular ring with a cross section similar to a trough, in which is placed the steel scrap forming a continuous ring or circuit. The ring is horizontal and is surrounded vertically with a laminated core on the outside as well as through the center—the two being connected across the top and bottom. A circular copper ring operating on a low-frequency power circuit serves as the primary of a transformer with the ring of scrap steel acting as a secondary. Here again the resistance of the steel charge to the flow of the generated current develops sufficient heat to melt the scrap. One furnace of the type of 6-ton capacity is in service at present.

With furnaces of the induction type, the metal is in constant motion and it is difficult to maintain a protective slag. Where such protection is required, it is generally necessary to employ inert or reducing gases as an atmosphere covering the metal.

Both types of induction furnaces serve an admirable purpose in remelting chrome steel scrap. Practically no chromium is lost and nearly the entire alloy content recovered with very little or no other pollution. It is, therefore, only necessary to remelt, add a slight amount of alloy as required and again pour into ingots for rolling.

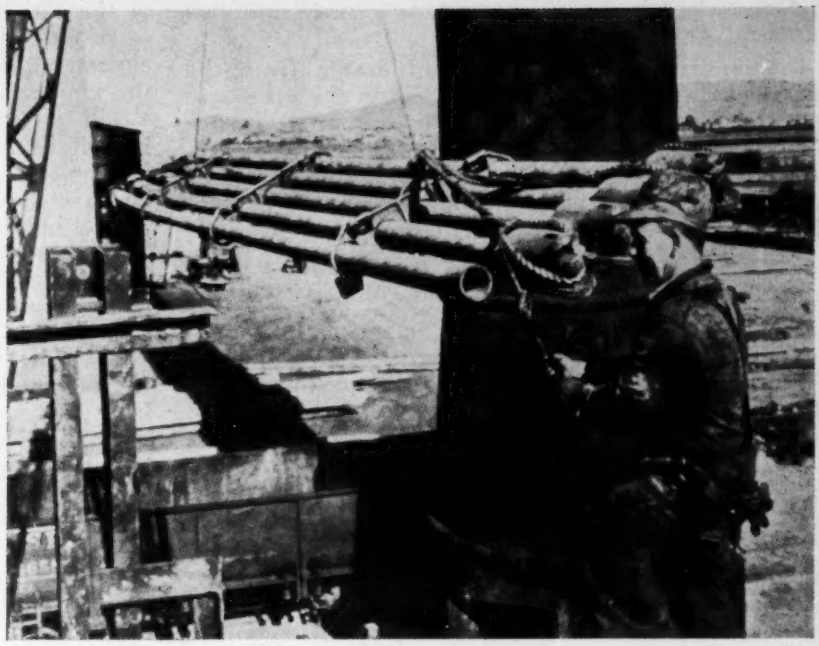
The rolling practice employed on these intermediate chrome alloys is quite similar to the general alloy steels. The temperatures are a little lower on the mills and special attention is paid to removal of surface defects at each conversion or re-rolling. The ingots are first rolled to slabs or billets. These are carefully inspected, chipped or ground and billets re-rolled to tube rounds or various bar sizes, while the slabs are rolled to sheets or plates. The tube rounds are pickled to facilitate inspection and either chipped or ground before shipping to the tube mill. Sheets and light plates are rolled to an intermediate break-down where they are again pickled and ground to remove defects and then rolled to finished size. Sheets and plates are cooled from the mill and annealed for softening by slow cooling from about 1600° F. to a Brinell hardness of about 170 or less. Rounds and bar stock are slowly cooled from the mill and either supplied hot rolled in the case of tube rounds, or annealed or heat treated for general bar stock.

STAINLESS STEELS

The stainless steels are a group of alloys containing chromium or chromium and nickel, generally with low carbon and with or without other elements. They are conveniently divided into two types, known as the straight chrome and chrome-nickel groups.

The first or chrome group contains 12 percent or more of chrome. The 12-14 percent chrome is the most commonly used of this type in refinery equipment. It may contain low carbon, under .10 percent, for sheet products or higher amounts, up to .40 percent, where hardness is desired. In sheet form, either with or without moly, it has been used successfully as liners for reaction chambers and other equipment where lower alloys do not possess sufficient resistance to corrosion. In bar form it is heat treated and used in pump parts, valves, etc., where corrosion resistance and same abrasion is a factor. These alloys are magnetic, are air hardening on welding, can be heat treated, are ferritic and have a coefficient of expansion about the same as common steel.

The second group contains 16 percent or more chrome and 6 percent or more nickel with or without other alloys. The most common of this group is 18-8 with low carbon, under .07 percent. This has given



After 40,000 hours of service in an oil cracking plant, these Enduro tubes were in such good condition that they were reinstalled in new supports.

very satisfactory results in service as still tubes. It possesses very good creep strength, about four times that of carbon steel at elevated temperatures, around 1100 to 1400° F. Tubes of this analysis have been used for 6 to 8 years and are still good. A modification of this analysis, containing in addition about 3 percent moly, has very high resistance to such acids as sulphurous and phosphoric and many others. It is being used more extensively right along for such service where acid resistance is necessary. The chrome-nickel corrosion resistant alloys are austenitic or non-magnetic and cannot be hardened by heat treating, have a high coefficient of expansion, are tough and ductile and well adapted to welding. In many instances 18-8 coated welding electrodes are used for arc welding the straight chrome alloys in refinery and other equipment.

These stainless alloys are all made in the electric furnace and poured into various sized ingot molds from small 10 x 10-inch up to very large ones weighing 60,000 pounds for large and heavy plates. Both types of steel are heated in ingots to 2150-2300° F., and rolled to slabs or billets. These are carefully inspected and ground to remove surface defects. Slabs are then rolled to plates or break-downs and again ground before final rolling to sheet or light plates. Rolling temperatures for these conversions will average about 1850° F. for chrome-nickel and 1500° F. for the straight chromes. The lower temperature for the latter being necessary to develop proper structure and physical properties. Billets are re-rolled to tube rounds or commercial bar stock. Tube rounds are rough turned over their entire surface to remove all surface imperfections before shipping to the tube mill. Bar stock is annealed or heat treated. The straight chrome is annealed at 1450 to 1500° F., and the chrome-nickel at 1900 to 1950° F. The former can be slowly cooled but the latter should be quenched if possible.

Both types are rolled into hot- and cold-rolled strip and sheets, either plain white pickled or polished to various degrees of reflectivity.

HEAT RESISTING ALLOYS

The heat resisting steels are quite similar to the stainless products, except they are more highly alloyed. They contain up to 30 percent chrome in the straight chrome group and 25 percent chrome, 20 percent nickel, or up to 80 percent nickel and 20 percent chrome in the chrome-nickel group. These are used for resistance to scaling at high temperatures such as furnace parts, tube supports, etc. The chrome-nickels possess the most strength, but the straight chromes are most desirable where high sulphur is encountered.

These alloys are similar in physical properties to the stainless alloys and are all made in the electric furnace. As a rule they are cast into small ingots, such as 8 x 8-inch up to 20-inch rounds. They are quite sensitive in the ingot form and are forged to slabs and billets rather than rolled, as the working temperature range is narrow and frequent reheating is necessary. The forged billets and slabs are ground free of defects and rolled to smaller sections in bar sizes or sheet and strip.

PIERCING MILLS

The tube rounds are pierced in mills having different types of piercing and rolling equipment. The tube rounds are heated to piercing temperature in furnaces which are inclined to permit continuous rolling of the billets from the cold end of the furnace to the hot zone. The heating times and temperatures are dependent upon the type of equipment and upon analysis ranging from 2200 to 2300° F. The heated rounds pass through the piercing rolls, either Mannesman type or Steifel discs, which rapidly reduce the diameter of the round and then cause the metal to flow over a point, thus producing a pierced hollow. The setting of the rolls will control the wall thickness, while the guides will control the outside diameter. The pierced hollow then passes through a two-high mill, using a plug on the inside. This operation reduces size and wall thickness and eliminates the piercing mill marks. The rolled tube is then given a pass through another set of rolls, which rapidly revolves the tube and makes the outside diameter uniform. The tubes may be reheated and sent through a series of rolls, which reduces the outside diameter, or the tubes may go directly through a series of rolls for sizing pass to make the outside diameter still more uniform.

The carbon steel tubes of low carbon content will be soft coming from the hot mill and can be easily fabricated. The alloy tubes of 4-6 percent chrome series will require an annealing treatment to make them soft. Usually this annealing temperature is 1525 to 1575° F., cooling slow enough to get desired hardness under 179 Brinell. Scale can either be removed by pickling or sand blasting. The 18-8 analysis is usually annealed at about 1850 to 1950° F.,

and quenched in water to produce a small uniform autenitic grain structure.

Condenser tubing will be cold drawn from the annealed and pickled material. Since the sizes are small, a number of cold drawing passes are necessary so that intermediate annealing and pickling is required between drafts. The annealing temperatures will be low for the plain chrome series (4-6 percent chrome group and 16-18 percent chrome).

IMPACT TESTING

The impact test is used as an index of the toughness of metal under dynamic shock. The effects of alloying elements to carbon steels and the effects of temperature upon the impact properties are of vital interest to the refinery. It is conceded that the Charpy Keyhole Notch Impact specimen is the one in general use and the following remarks are based upon results obtained with this test specimen.

If the part is to be used at room temperature, then much depends upon the size and service. As the size increases and as higher strengths with high impact are demanded, suitable alloying elements must be added.

Where parts are subjected to both elevated and room temperatures, the problem of temper brittleness enters. There are two temper brittle ranges which more or less merge into each other. The first takes place between 850 and 1025° F., and its amount is increased as the tempering time is increased. It is not affected by the rate of cooling. The second temper brittleness occurs about 1025° F., and its susceptibility is affected markedly by the rate of cooling and increased slightly with tempering time. Slow cooling increases the second temper brittleness.

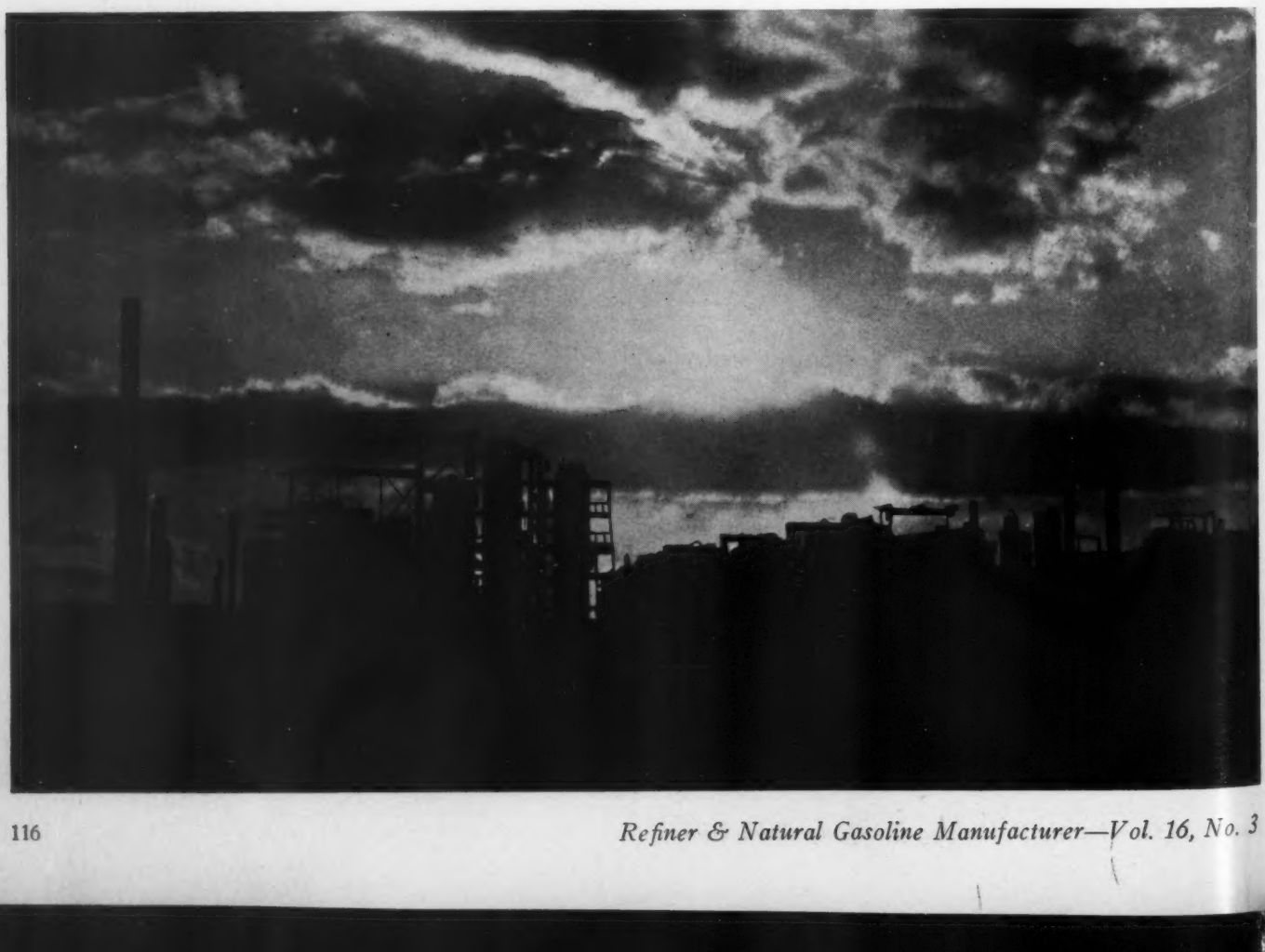
The first case is believed due to carbide precipitation and the second case depends upon the solubility of the carbide with increasing temperature and rate of cooling to prevent reprecipitation. The elements, chrome, manganese, phosphorus and sulphur increase the temper brittleness in proportion to their amount. While the elements tungsten, moly, vanadium, titanium and columbium reduce the tendency to temper brittleness. Carbon steels are not temper brittle because they precipitate their carbide below 580° F. Nickel increases the susceptibility only very slightly, but accentuates this effect when in combination with chromium. Thus, molybdenum is added to chrome and chrome-nickel steels to reduce their temper brittleness.

For low temperatures best results are obtained from quenched and highly drawn specimens which have maximum grain refinement. For hot-rolled or normalized mild-carbon steels the low temperature impact strength increases with decreasing oxygen content of the steel. Herty reports the order of resistance to low temperature 32° F. to 40° F., embrittlement is as follows:

(a) Thoroughly killed steels containing definite amounts of aluminum in solution—best.
(b) Semi-killed steels to which aluminum has been added.
(c) Silicon killed steels.
(d) Rimmed steels—poorest.

For alloy steels at low temperature, nickel, vanadium and moly favor higher impact values. The smaller the grain the higher the impact resistance. Cold working increases the susceptibility.

Blue brittleness is found in highly quenched and strained gear steels which have been drawn between 400 to 650° F. The chrome and chrome-nickel oil hardening steels are highly susceptible. The nickel-moly, nickel and chrome-nickel-moly are only slightly susceptible and are preferred where shock resistance is paramount.



Intermediate Alloy Steels

For High Temperature Application

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THE advance in refining technology has been extremely rapid during the past few years and has brought technical problems in tube manufacture and design to the special attention of refinery designers. This has led to a study of the economic value of various steel analyses, for in the face of possible technical obsolescence before the economic value of equipment has been obtained, the problem of decision has been difficult. High temperature studies by Timken at the University of Michigan and in its own laboratories have furnished much valuable data on corrosion, oxidation and creep strength which can be used by designers.

Alloy steels for refinery service now are being designed on an economic basis. Certain alloy additions are intended to increase corrosion or oxidation-resistance rather than creep strength, for in some cases these qualities control the efficiency of the design as a whole. Chromium is used to provide corrosion resistance. Silicon increases oxidation resistance. Molybdenum acts to inhibit temper brittleness as well as to increase creep strength. In the 4-6 percent Cr-Mo steels small amounts of titanium or columbium act to prevent air hardening.

Steels containing up to 2 percent of chromium apparently show a greater resistance to corrosion in proportion to their chromium content than do those in which larger percentages have been used, the corrosion resistance being proportional to the amount of chromium present in the range between 3 and 10 percent of Cr.

Economic balance between life, service and cost may frequently be obtained in the case where plain carbon steel tubes are not entirely suitable, yet where 18-8 steel tubes are too expensive, by using an intermediate or low alloy steel. 4-6 percent Cr steel with 0.50 percent molybdenum usually lasts approximately five times as long as carbon steel in cracking furnace tubes. Timken DM steel, which has 1.00-1.50 percent of chromium combined with 0.50 percent of molybdenum, may be expected to give from two to three times the life of plain carbon steel. The Sicromo 1, 2 and 3 steels, carrying varying amounts of chromium and silicon, are intermediate molybdenum steels between DM and the 4-6 percent Cr alloys. In some liquid and vapor phase applications the rate of corrosion of these steels is nearly as low as in the 4-6 percent Cr-Mo steel.

Both silicon and aluminum have demonstrated their value in increasing the oxidation resistance of steels containing chromium. Silicon alone will protect plain carbon steels against serious oxidation up to 1200-1250° F., and where chromium is added this effect carries on to still higher temperatures. Tests show that 2 percent of silicon in a 6 percent chromium steel will assure approximately the same resistance to oxidation in air as is developed by a 25 percent Cr steel at 1500° F.

A 4-6 percent Cr-Mo steel with 0.50 percent of silicon shows reasonably good resistance up to 1250° F. The Sicromo 1, 2, 3 and 5 steels all show substantial increases in oxidation resistance at 1000°, 1250° and 1500°F. No chromium is used in Silmo, yet at 1200°F. this steel shows approximately the same resistance to oxidation as does the 4-6 percent Cr-Mo steel. The comparative oxidation resistance of these various low and intermediate alloy steels is shown in the accompanying table.

Another factor in favor of low and intermediate

Loss in weight in grams per square inch of original surface after 1000 hours continuous heating in air.

STEEL	1000°F.	1250°F.	1500°F.
Carbon	0.06	1.95	5.61
Car-½ Mo	0.06	2.03	5.79
Silmo	0.05	1.06	4.64
DM	0.05	1.49	4.67
Sicromo 1	0.05	0.93	3.40
2 Cr-Mo-Ti	0.05	0.64	4.92
Sicromo 2	0.02	0.72	0.88
Sicromo 2½	0.03	0.81	4.05
Sicromo 3	0.01	0.08	0.19
5% Cr-Mo	0.03	0.65	4.99
5% Cr-Mo-Ti	0.02	0.58	2.40
Sicromo 5	0.01	0.03	0.04
18-8 Stainless	0.00	0.01	0.03

alloy steels is their quality of swelling or bulging prior to bursting. This serves as a warning and tends to avoid accidents, an important item in refinery operation.

Creep strength may be improved by the use of molybdenum, tungsten, vanadium and chromium either alone or preferably in combination and by the proper balancing it has been possible to combine good creep strength with satisfactory oxidation and corrosion resistance.

The addition of approximately 0.50 percent of molybdenum is regarded as a standard in the steel industry for increasing the creep strength of steels for use in refinery tubing. Tungsten and vanadium are effective between 800-1200°F. but their cost is still too high to enable these elements to be used in a sufficient quantity for best results. In the temperature range 800-1200°F., chromium reaches a maximum in its effect upon creep strength at 1.00-1.25 percent addition.

Design engineers must balance first cost, creep strength, corrosion and oxidation resistance as they apply to the particular problem at hand. For some applications, plain carbon steel tubes will be sufficient. In other cases the higher creep strength, longer life, greater safety, and lower maintenance cost of alloy steel tubing is sufficiently important to offset the higher cost of such equipment. The accompanying table presents a broad summary of these various properties for a wide range of the steels now commonly used.

Carbon-molybdenum steel, for example, shows a satisfactory creep strength up to 1100°F. but has a slightly greater oxidation loss than plain carbon steel. Silmo may be used to replace carbon steel where greater safety is desired, or as a substitute for Carbon-moly where oxidation is a problem. Its creep strength is about twice that of carbon steel at 900-1100°F. and its oxidation resistance compares favorably with that of 4-6 percent Cr-Mo steel. However, its corrosion resistance is about the same as that of carbon steel.

DM steel has found a place during recent years, having high creep strength between 900-1100°F. combined with approximately two to three times the oxidation and corrosion resistance of plain carbon steel. The series of Sicromo steels offer still other favorable analyses where additional corrosion resistance is required and where the resistance to oxidation is of major importance.

Where extremely high creep strength is not required, yet good stability together with high oxidation and corrosion resistance is essential, the 4-6 percent Cr-Mo steel is particularly suitable. Service data indicate that tubes made from this steel will last approximately five times as long as plain carbon tubes in cracking still service. Where maximum oxidation resistance is essential, Sicromo 5 steel, which compares favorably with 18-8 steel up to 1500° F., may be employed to great advantage. Its corrosion resistance and creep strength compare favorably with 4-6 percent Cr-Mo steel.

When selecting tubes for use in refinery service it is essential that service requirements be studied in connection with the properties of the steels available. Maximum efficiency and economy may frequently be secured by selecting different steels for different locations in the same furnace. No one steel is most suitable for all applications.

Thus it will be seen that best results and maximum economy may be secured by cooperation. The tube manufacturer, the designer and the user should all cooperate in solving the technical problems now involved in refinery design. A slight modification in design may mean a major change in the conditions under which the tubes must function, or the use of a different alloy than the one first contemplated may mean a substantial reduction in operation and maintenance costs.

Metallurgical research is continuing abreast of chemical research in new refining practices. New methods bring new problems, and the designer must coordinate the data at hand. Service data and laboratory results are constantly being studied by metallurgists and they are glad to cooperate with designers and users in applying their information to the solution of the technical and economic problems involved in the design and operation of modern refining equipment.

Comparative Data

Service Temperature	Steel Recommended	Creep Strength	Oxidation Resistance	Oil Corrosion Resistance
Up to 900°F.....	Carbon.....	C	B	D
900-1000°F.....	Carbon-moly..	B	B	D
	Silmo.....	C	B	C
	Sicromo 1....	C	B	B
	Sicromo 2....	C	A	B
	DM.....	A	B	C
	Sicromo 2½..	C	B	B
	Sicromo 3....	C	A	A
	4-6% Cr-Mo..	C	B	A
1000-1100°F.....	Carbon-moly..	B	D	D
	Silmo.....	C	B	D
	Sicromo 1....	C	B	B
	Sicromo 2....	C	B	B
	DM.....	A	C	C
	Sicromo 2½..	C	B	B
	Sicromo 3....	B	A	A
	4-6% Cr-Mo..	B	B	A
	Sicromo 5....	B	A	A
1100-1200°F.....	Silmo.....	D	B	D
	Sicromo 1....	C	B	C
	Sicromo 2....	C	B	B
	Sicromo 2½...	C	B	B
	Sicromo 3....	C	A	B
	4-6% Cr-Mo..	C	B	A
	Sicromo 5....	C	A	A
1200-1300°F.....	Sicromo 3....	D	B	B
	Sicromo 5....	D	A	A
	18-8 Stainless.	A	A	A

Code: A—Excellent. B—Good. C—Fair. D—Low.

Copper *and* Copper-Base Alloys

In the Construction of Corrosion-Resisting Equipment and Structures

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COPPER AND copper-base alloys have been used extensively in industry for centuries.

In general, the physical and chemical properties of these materials are well known and much published information pertaining to their resistance to corrosion is readily available to the engineer. Most of the available information on corrosion resistance, however, is based on laboratory observations. In the laboratory it is a relatively simple matter to determine the resistance of a given metal or alloy to the corrosive attack of a specific reagent under stated conditions of temperature and concentration. When in a particular instance published information is not available, laboratory data of this fundamental and important type can usually be readily developed.

In the field, however, it does not suffice to consider only the chemical action of a given corrosive agent on a specific metal or alloy. It is necessary also to consider the influence of numerous other possible factors affecting corrosion, which may be incident to industrial application of that metal or alloy. Impurities present in either the agent or metal are frequently sources of destructive corrosion of a metal that normally would be unaffected, if it or the agent were pure. The effect of atmospheric oxygen in conjunction with the agent, the conditions existing by reason of agitation or flow of fluids, and many other secondary factors, must be taken into account by the engineer in selecting a suitable corrosion-resisting material of construction. In addition, the physical condition and the physical properties of the metal, and even the methods employed in its fabrication, must be considered, for all these are factors which may affect its resistance to corrosion.

Furthermore, the selection of a suitable corrosion-resisting material for an industrial use demands careful consideration of many economic factors. The engineer in any ordinary case obviously seeks the material which will give him the maximum service per dollar of investment, and he should balance material costs, construction costs, replacement and shutdown costs in an effort to determine which available material of construction will, in a given application, show him the maximum economic advantage.

In many industrial applications, copper and its numerous alloys are substantially immune to the corrosive action of the media to which they are exposed, and will last indefinitely. There are other industrial applications where these metals should give an indefinitely extended service, but where failure because of corrosion may result by reasons of unsuitable design and improper mechanical construction. Further, there are many situations in which no commercial metal will have an indefinitely longe life, but in which copper and its alloys possess a combination of physical and chemical properties which render them the best obtainable materials, when all factors, including ultimate costs, are taken into consideration. It is particularly true that design and operating factors must be given the closest attention in connection with applications of these two latter kinds, and, commonly, careful control of such factors, when possible, will result in successful and satisfactory performance in many instances where rapid deterioration of the metal might otherwise occur.

The foregoing considerations are not peculiar to copper and its alloys, but the same considerations, of course, are equally pertinent with respect to ferrous and other metals and materials subject to corrosion.

It is not the purpose of this paper to present an extensive tabulation of existing information on the resistance of copper and its alloys to a multiplicity of corrosive media. It aims rather to present the characteristic corrosion-resisting properties and the fundamental physical properties of the metals in question, and to direct the attention of the engineer to those easily overlooked factors which so often determine the effectiveness of a given cuprous material when used in a structure or apparatus designed to resist corrosion. In addition, it will discuss certain familiar applications of these materials, and those factors incident to such applications, which the engineer must take into account, if he is to secure maximum effectiveness of the corrosion-resisting properties of the materials. An understanding of these factors will aid his consideration of the problems arising in connection with analogous applications.

There are many copper-base alloys of industrial significance and, from the standpoint of the engineer, the materials under consideration in this discussion can be naturally classified in the following groups:

1 Copper.

2 The brasses, including not only the binary copper-

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zinc alloys, but those alloys as modified by the addition of small percentages of other constituents.

3 The copper-silicon alloys as modified in commercial practice by additional constituents.

4 The bronzes or copper-tin alloys and the aluminum bronzes.

5 Cupronickel and nickel silvers.

6 Those alloys used primarily for the production of castings and not normally susceptible of fabrication through hot-or-cold working.

COPPER

Copper is commercially available in a high degree of purity as electrolytic copper. In the United States this form of copper constitutes by far the bulk of that metal used in commercial products. For special purposes, however, there are available modified forms of copper, such as the arsenical coppers, the argentiferous coppers, phosphor deoxidized copper, oxygen-free copper, and fire-refined copper.

Except that arsenical coppers seem to retain their strength better at elevated temperatures than the others (1, 2, 3, 4, 5, 6), the chemical properties of these metals influencing their resistance to corrosion are so generally similar as to render separate discussion of each of them unnecessary.

VARIOUS FORMS OF COPPER

Commercial argentiferous copper contains up to approximately 12 ounces of silver per ton, and is used principally in applications where fabricated articles are to be assembled by a soldering operation. The silver content raises the softening temperature of the metal, and thus prevents annealing of the assembled parts in the solder bath (1, 7, 8, 9, 10, 11, 12). The silver, however, has no appreciable effect, one way or the other, in influencing the resistance to corrosion.

The arsenical coppers are not widely used in this country, although they are favored in England. It is the English opinion, substantiated by experience and some little experimentation, that the arsenical coppers are somewhat more resistant to corrosion than electrolytic copper (13-21 incl.) It would appear, however, that, even if this is true, the difference is nevertheless slight, and probably of but little commercial significance.

Arsenical coppers, however, are used to advantage where the material is to be exposed to relatively high temperatures. The presence of arsenic appears to inhibit scaling to some degree and for certain applications controlled quantities of arsenic are added to the copper. Most arsenical coppers contain moderate quantities of silver and there is some evidence that the silver so present, acting in conjunction with arsenic, is a factor in the reduction of scaling (2, 22, 23, 24).

The phosphor-deoxidized coppers are used for tubing and other applications where flaring, flanging, and spinning operations might be deleteriously affected by the presence of the copper-copper-oxide eutectic dispersion that is characteristic of electrolytic copper. The use of phosphor-deoxidized copper is advantageous when the metal is to be exposed in processing or service to the action of reducing gases at elevated temperatures. In such cases electrolytic copper is liable to embrittlement due to the deoxidization of the eutectic by the reducing gases (25, 26). The phosphor-deoxidized coppers also are preferable to electrolytic copper when welding operations are to be performed.

In recent years an oxygen-free coppr has been marketed, which presents the same advantages as already outlined for the phosphor-deoxidized coppers, and in addition, presents the advantage of unimpaired high electrical conductivity.

In standard commercial forms the phosphor-deoxidized and the oxygen-free coppers are in general more expensive than comparable forms of electrolytic copper and their use in preference to the electrolytic copper is, therefore, only warranted where a definite advantage is secured.

Fire-refined copper is seldom used in the United States in the production of the standard commercial wrought-metal forms. In this country fire-refined copper is usually sold in the form of ingots for the purpose of making copper and copper-alloy castings.

CORROSION-RESISTANT PROPERTIES OF COPPER

While there are certain differences as indicated in the common commercial kinds of copper, none of these modifications exerts a profound influence on the characteristics of the metal in respect to its ability to resist corrosion.

In general, it can be stated that copper withstands atmospheric corrosion and sea-water corrosion as satisfactorily as any commercially available metal, and it has been used for centuries in construction where resistance to attack of this nature is necessary. In addition, it can be stated that copper is substantially immune to the chemical attack of a large variety of industrial chemicals (27-39 incl.), although copper ordinarily should not be used in contact with oxidizing acids and most oxidizing agents, or in situations where alternate exposure to oxidizing conditions and acid reagents is anticipated (28, 40-44 incl.).

In the foregoing connections, and of considerable commercial significance, it should be recognized that the presence of relatively small percentages of certain metallic salts in solutions of nonoxidizing acids is likely to introduce rapid corrosive action. Metallic salts readily susceptible of chemical reduction are particularly dangerous in this respect; and ferric, stannic, mercuric, and cupric compounds, particularly, constitute a source of danger when present in an otherwise non-oxidizing acid solution, which of and by itself might be inactive with respect to copper (30, 31, 41, 45, 46, 47).

Ammonia and carbon dioxide are two commonly encountered substances, which in the presence of moisture and in relatively low concentration can constitute active corrosive agents with respect to copper (30, 35, 43, 48).

Copper is used in many forms and in many applications where its high thermal and electrical conductivities are of primary importance. In such situations its resistance to corrosion is a property of value, but commonly of somewhat secondary importance, and corrosion problems are not normally encountered in such fields.

As a material of construction, copper should be regarded as a metal having great resistance to corrosion under a wide range of conditions and rendered attractive to the engineer by its malleability, ductility, and the readiness with which it may be worked, formed, soldered, and brazed, and, under proper conditions, welded. Its physical properties, particularly with respect to tensile strength, are not impressive, and pure copper, where its use is based primarily on its resistance to corrosion,

TABLE 1

Physical Properties of the Brasses

MATERIAL	Tensile Strength, Lbs. per Sq. In.		Elastic Limit, Lbs. per Sq. In.		Elongation, Percent		Rockwell B Hardness		Melting Point, C	Density, Lbs. per Cu. In.	Coefficient of Expansion	Electrical Conductivity[1]	Thermal Conductivity[2]	Modulus of Elasticity, Lbs. per Sq. In.
	Hard	Soft	Hard	Soft	Hard	Soft	Hard	Soft						
Red brass (85 Cu, 15 Zn)	80,000	45,000	35,000	15,000	4.5	43	89	3	1020	0.316	0.0000187	37.0	0.38	15×10^6
70-30 Brass (70 Cu, 30 Zn)	95,000	53,000	91,000	16,000	7	51	93	15	955	0.308	0.0000199	27.58	0.290	15×10^6
High brass (65 Cu, 35 Zn)	93,000	51,000	73,700	18,500	2	50	90	30	930	0.306	0.0000202	26.8	0.285	15×10^6
Admiralty (71 Cu, 28 Zn, 1 Sn)	100,000	53,000	98,000	18,000	4	67	95	15	935	0.308	0.0000202	24.65	0.263	15×10^6
Aluminum brass (76 Cu, 22 Zn, 2 Al)	83,000	62,000	75,000	16,000	5	52	86	33	970	0.301	0.0000185	22.56	0.240	15×10^6
Muntz metal (60 Cu, 40 Zn)	88,000	59,000	82,000	15,000	5	52	91	24	905	0.304	0.0000208	28.60	0.300	15×10^6
Commercial bronze (90 Cu, 10 Zn)	67,000	37,600	55,000	15,000	3	40	75	1	1045	0.318	0.0000182	40.90	0.446	15×10^6
Roman or Tobin bronze (60 Cu, 39.25 Zn, 0.75 Sn)	90,000	54,000	70,000	15,000	4	40	93	55	885	0.304	0.0000211	24.93	0.279	15×10^6

Data based on information published by the Revere Copper and Brass, Inc., American Brass Company, and Chase Brass and Copper Company.
[1] Percent of International Annealed Copper Standard.
[2] Cal. per sq cm per cm per sec per C at 20 C.

is usually employed only as a covering or lining, rather than as a basic material of construction. An outstanding exception, however, to this general statement is the case of tubes and pipes where adequate strength to meet service conditions is readily obtainable because of the strength inherent in the shape of a tubular article.

Because of its physical and chemical characteristics copper is frequently used as a base for applied coatings. Typical of such products is tinned copper, which finds application in many industries where the presence of bare copper for one or another reason may be objectionable.

BRASSES

The most widely used and the best-known copper-base alloys are the brasses. These are basically binary alloys of copper and zinc, but in many instances certain of their physical and chemical properties are modified or controlled by intentional additions of small amounts of one or more other metallic constituents.

As a rather broad generality, it might be said that brasses are used by the engineer in applications where it is desired to improve upon a basic characteristic of copper, and where such improvement may be effected at a sacrifice only of such other characteristics of copper as are unimportant in respect to the particular application at hand.

Among the brasses we find alloys which are markedly stronger than copper, and in consequence can be used more satisfactorily than the latter in structural applications. Such alloys retain a resistance to corrosion adequate to meet the requirements of many widespread uses. Indeed, with respect to certain specific causes of corrosion, certain of the brasses are more resistant than the parent metal itself (29, 30, 53-58 incl.). This latter is particularly true where so-called "impingement corrosion" or erosion is involved; but it is seldom that a brass is actually more passive than copper itself.

Commonly, certain mill products and certain manufactured products may be produced at less cost if, instead of copper, certain of the brasses are used, and, obviously, therefore, cost frequently is the consideration which leads to the use of brass rather than copper for a given product.

It is true that, where a brass alloy offers an advantage over the parent metal, that advantage is usually had at the sacrifice of both electrical and thermal conductivity, but it is equally true that these two latter properties are commonly of negligible significance in many applications where corrosion resistance is desirable.

Brasses are manufactured commercially in a range of composition running from approximately 95 percent copper and 5 percent zinc down to 55 percent copper and 45 percent zinc. Within this range of composition as modified by the addition of numerous other constituents, there are literally hundreds of commercial brass alloys of varying composition and properties.

CHARACTERISTICS OF THE IMPORTANT BRASSES

It would be impossible within the scope of this paper to give detailed and specific information with respect to each commercial brass alloy. Table I lists the more important commercial brasses and gives their composition and fundamental properties. Figs. 1, 2, and 3 illustrate graphically variations of certain physical characteristics of typical brass alloys, capable of being secured by a control of mill operations. Table 2 lists general information with respect to the corrosion resistance of the more important brasses.

The tables given, and the references cited, present detailed information sufficient to answer any usual question that might be asked with reference to the performance of a given brass in contact with a definite corrosive substance. There are, however, in this respect

TABLE 2

Corrosion Data—Brasses—Rates Expressed as Penetration in Inches Per Year, Ref. (79)

TEST No.	1	2	3	4	5	6	7	10	10A	11	12	13	14	15
Red brass (85 Cu, 15 Zn)	0.0005	0.0015	0.0019	nil	0.0025	0.0087	0.0852	0.0343	0.0065	.....	0.0001	0.0153	0.0027	.....
Two-and-one brass (67 Cu, 33 Zn)	nil	0.0019	0.0029	0.0002	0.0018	0.0068	0.0005	0.0293	0.0069	.....	.....	.....	.....	0.0296
Tobin or Roman bronze (60 Cu, 39 Zn, 1 Sn)	nil	0.0028	0.0030	0.0001	0.0022	0.0034	0.0002	.....	.....	.....	.....	.....	.....	.....
Naval brass (cold roll) (63 Cu, 35 Zn, 2 Sn)	nil	0.0039	0.0026	0.0002	0.0029	0.0014	0.0004	0.0539	0.0045	.....	.....	.....	.....	.....
Naval brass (hot roll) (63 Cu, 35 Zn, 2 Sn)	nil	0.0030	0.0038	0.0001	0.0018	0.0021	0.0003	.....	.....	.....	.....	.....	.....	.....
Muntz metal (cold roll) (60 Cu, 40 Zn)	nil	0.0039	0.0027	0.0001	0.0023	0.0035	0.0003	0.1579	0.0068	.....	.....	.....	0.0024	.....
Muntz metal (hot roll) (60 Cu, 40 Zn)	0.0001	0.0047	0.0025	0.0001	0.0033	0.0028	0.0004	.....	.....	.....	.....	.....	.....	.....
Admiralty (cold roll) (70 Cu, 29 Zn, 1 Sn)	nil	0.0016	0.0017	nil	0.0044	0.0030	0.0008	.....	.....	.....	.....	0.0092	0.0027	0.0316
Admiralty (hot roll) (70 Cu, 29 Zn, 1 Sn)	nil	0.0027	0.0023	0.0001	0.0028	0.0083	0.0012	0.0349	0.0058	.....	0.0001	0.0084	0.0038	.....
Manganese bronze (cold roll) (56 Cu, 41 Zn, 1 Al, 1 Fe, 0.5 Sn, 0.5 Mn)	nil	0.0022	0.0028	0.0002	0.0015	0.0025	0.0004	.....	.....	.....	.....	.....	.....	.....
Manganese bronze (hot roll) (56 Cu, 41 Zn, 1 Al, 1 Fe, 0.5 Sn, 0.5 Mn)	nil	0.0026	0.0034	0.0002	0.0022	0.0018	0.0003	.....	.....	.....	.....	.....	.....	.....
Manganese bronze (cast) (58 Cu, 38 Zn, 1 Sn, 1 Fe, 1 Pb)	nil	0.0027	0.0034	0.0001	0.0027	0.0029	0.0003	.....	.....	.....	.....	.....	.....	.....
Copper	0.0025	0.0029	0.0012	nil	0.0244	0.0506	100%	0.0515	0.0069	0.0001	0.0002	0.0088	.....	0.0208

Corrosion rates are average. For test conditions see Table 10.

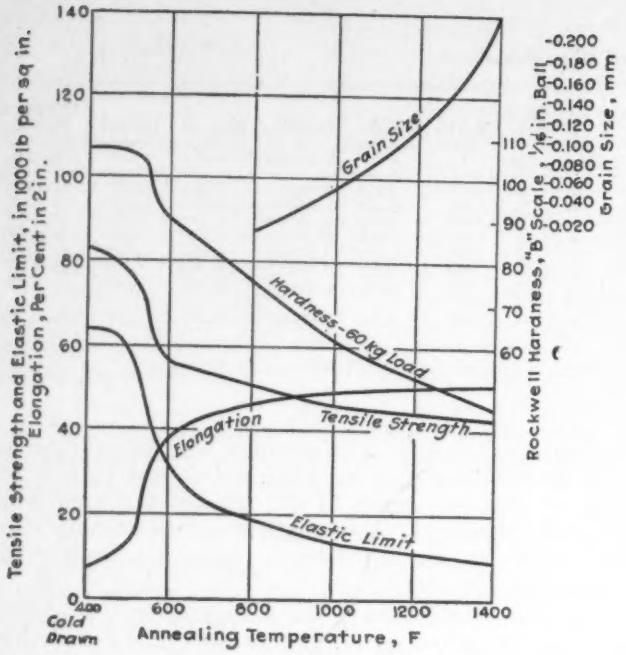

FIGURE 1

Physical properties of 80-20 brass sheet. (Cold-rolled 4 B. & S., numbers hard to 0.042 in. and annealed as shown.)

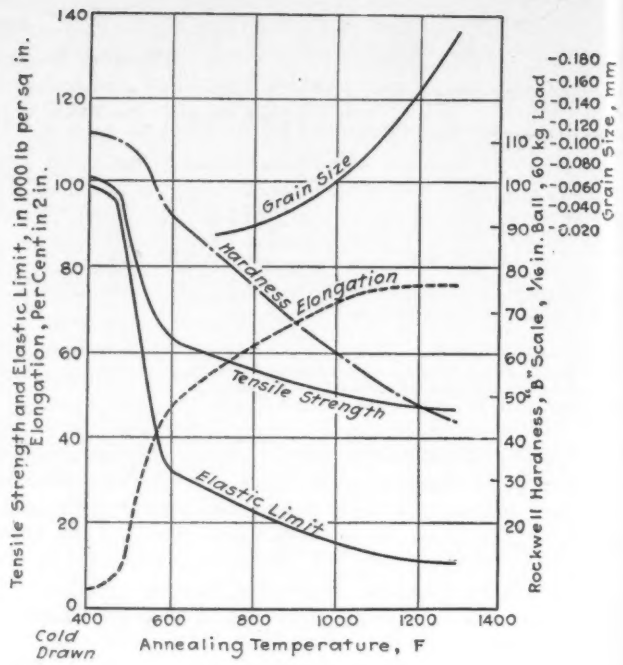

FIGURE 2

Physical properties of Admiralty condenser tubing. (¾ in. outside diameter x 0.049 in.)

certain general characteristics of this type of alloy that can be usefully discussed.

First, brasses having from nearly 100 percent down to 64 percent copper are structurally a single-phase solid solution of zinc and copper. This is termed the "alpha" phase. Below 64 percent copper, a second or "beta" phase appears, and the commercial alloys ranging from this copper content downward exhibit a mixture of the two phases and are known as the "alpha-beta" brasses. As the copper content decreases, the beta phase predominates and the alloys rapidly become brittle and valueless structurally. In the binary copper-zinc alloys the maximum ductility will be found in the alloys having in the neighborhood of 70 percent copper, and the maximum strength will be found in the alloys having from 60 to 63 percent copper, in which latter case the beta constituent is effective in hardening and strengthening the alloy.

Lead is frequently added to brasses to increase their machinability. In the case of the alpha-beta brasses the presence of lead does not affect, in any material way, the cost of mill processing. In the alpha range, however, lead, even in small amounts, does increase the difficulty and expense of the fabricating operations. Lead is not soluble in the brasses, and has little significant effect on their resistance to corrosion.

Manganese and iron are occasionally used as additions to alpha-beta brasses for hardening and increasing the strength of the product. Although there is some evidence tending to establish that such additions exert an unfavorable influence on the resistance of the alloy to corrosive attack, such influence, if it exists, is relatively minor (33, 34, 35, 53, 54, 59-63 incl.).

Additions of tin and aluminum, on the other hand, although having but minor effects on the physical properties of brasses, exert a pronounced effect in increasing the resistance to certain kinds of corrosion, which will be discussed later.

Many applications of brasses are determined by their ready machinability, the ease with which they can be drawn, spun, or stamped, or by reason of some other mechanical characteristic, in addition to their satisfactory resistance to moderate corrosive action.

RESISTANCE OF BRASSES TO CORROSIVE ACTION

In general, we seldom find brasses successfully used in direct contact with active chemical substances. Their useful field of application, in respect to corrosion resistance, is to products in which resistance to atmospheric corrosion, or the corrosive action of industrial or domestic waters, is desirable or necessary, and to articles and apparatus subject to the action of chemically neutral or basic substances relatively mild in corrosive action (55, 91).

Brasses for the most part are adversely affected by the same substances which have an adverse effect on copper, and in numerous instances are corroded by substances, particularly those which might be termed active chemical reagents, which do not affect copper to any appreciable extent. A noteworthy exception to this generality is that in resisting the corrosive attack of sulphides the brasses, on the whole, are better than copper, and their superiority in that respect becomes more marked as the zinc content increases (64, 117). Further, it is of particular interest, that in combating the corrosion of sea water, especially when such corrosive attack is aggravated by the action of atmospheric oxygen or complicated by conditions which introduce impingement attack or erosion, certain of the modified brasses, for example, aluminum brass, Admiralty metal, and possibly 85/15 brass (known as "red brass"), give materially better service in respect to withstanding corrosion than copper itself (65, 66, 67).

Brasses containing less than 85 percent copper when exposed to acidic media frequently fail in a characteristic manner termed "dezincification." Failures of this kind are identified by the appearance of spongy areas of copper in the form of either layers or so-called "plugs" on the affected surface. This spongy copper is a consequence of the solution of fractions of the alloy in the media and a redeposition of the copper by chemi-

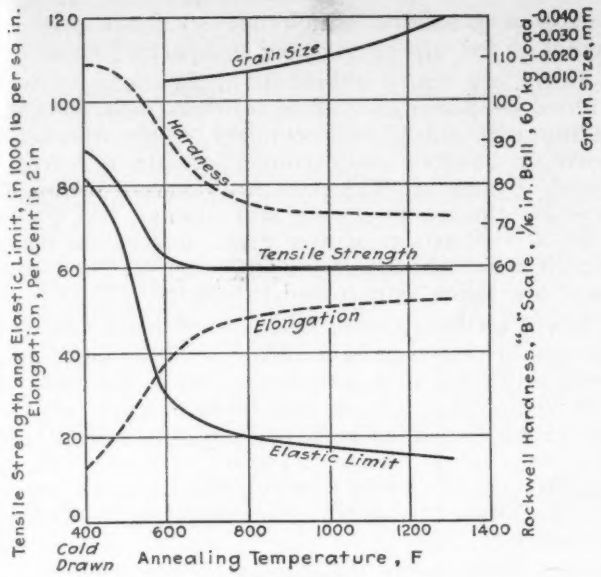

FIGURE 3

Physical properties of Muntz-metal condenser tubing. (¾ in. outside diameter x 0.049 in.)

cal displacement. Generally speaking, dezincification is confined to the brasses of higher zinc content, while those of higher copper content, such as 85/15 brass, commonly give satisfactory service in applications where the former are prone to failure through dezincification (55, 68-76 incl.).

Admiralty metal, in which 1 percent of tin is substituted for an equal amount of zinc in 70/30 brass, appears to be effective in respect to a reduced tendency toward dezincification; and this alloy has found widespread application, particularly to condenser tubes (55). To a certain extent this same effect of tin in reducing the tendency toward dezincification is noted in the alpha-beta range of brasses, and the alloy of 60 percent copper, 1 percent tin, and 39 percent zinc, which is of this type, has been used in the manufacture of marine shafting for many years. Naval brass is a generic term for this last-mentioned alloy. When prepared from materials of especially high purity and fabricated by methods which increase resistance to corrosion fatigue, the alloy is ordinarily offered under various trade names, such as Tobin bronze, Roman bronze, etc.

Arsenic in small fractional percentages is demonstrably effective in repressing or inhibiting dezincification in the brasses of higher zinc content. It is becoming rapidly recognized that good metallurgical practice calls for the presence of small fractional percentages of arsenic in brass condenser tubes (55, 77, 78).

One of the principal industrial applications of the brasses is to pipes and tubes to serve in condensers, heat exchangers, evaporators, and similar types of equipment and to serve as conduit for industrial waters, sea water, and industrial wastes.

In such uses active chemical attack is seldom to be anticipated. The engineer in attempting to determine which metal or alloy will show the longest life and the maximum economic advantage must give careful consideration to his operating conditions and their probable influence on the various materials of construction being considered. Such factors as operating temperatures, the presence, or absence, of entrained air, and circulating velocities, all vary from one installation to another and profoundly influence the performance of a given tube in contact with a given fluid.

In this connection it is important that the designing engineer recognize that there are many varieties of brasses, each possessing distinctive characteristics, and that in a given installation under specific conditions of operation it is entirely possible that while one kind of brass might give absolutely satisfactory service another kind might fail rapidly and completely. Further, it should be recognized that there are many copper-base alloys other than brasses, particularly designed to meet severe corrosive conditions, and that the engineer's range of choice is, therefore, by no means restricted to the copper alloys containing zinc. These other copper-base alloys, principally the copper-silicon alloys, the tin bronzes, the aluminum bronzes, cupronickels, and nickel silvers, will now be discussed.

COPPER-SILICON ALLOYS

While copper is in genedal use in the chemical and processing industries as a material for tank construction, sheathing, and similar applications, the brasses, in spite of their improved structural characteristics as compared to copper, are not commonly used for these purposes. The reason for this is that the improved physical properties of the brasses ordinarily are secured at a partial sacrifice of the resistance to corrosion that is a characteristic of copper.

Within recent years the copper-silicon alloys have been commercially developed and offer a material of high strength as well as excellent resistance to corrosion. These alloys in general possess a resistance to corrosion which is the equivalent of and is similar to that of copper. Indeed, in some instances and applications their corrosion resistance exceeds that of copper (28, 54, 61, 62).

In general, the copper-silicon alloys combine with the corrosion-resisting properties of copper physical properties and structural qualities quite comparable to those of mild steel. Inasmuch as they combine excellent structural properties and corrosion resistance in one alloy, they are of considerable importance to the engineer dealing with corrosion-resisting equipment (80, 81, 82).

It seems unnecessary in this paper to tabulate separately corrosion data for the copper-silicon alloys. From the standpoint of practical engineering it is safe to assume, from a corrosion point of view, that

TABLE 3

Physical Properties of the Silicon Bronzes

MATERIAL	Tensile Strength, Lbs. per Sq. In.		Elastic Limit, Lbs. per Sq. In.		Elongation, Percent		Rockwell B Hardness		Melting Point, C	Density, Lbs. per Cu. In.	Coefficient of Expansion	Electrical Conductivity[1]	Thermal Conductivity[2]
	Hard	Soft	Hard	Soft	Hard	Soft	Hard	Soft					
Silicon bronze, type A	120,000	67,000	103,000	24,000	10	60	99	65	1000	0.308	0.000017	8.07	0.086
Silicon bronze, type B	90,000	42,000	80,000	12,000	10	60	84	20	1030	0.313	0.000017	11.0	0.116

Data based on information pyblished by Revere Copper and Brass, Inc., American Brass Company, and Chase Brass and Copper Company.
[1] Percent of International annealed copper standard.
[2] Cal. per sq cm per cm per sec per C at 20 C.

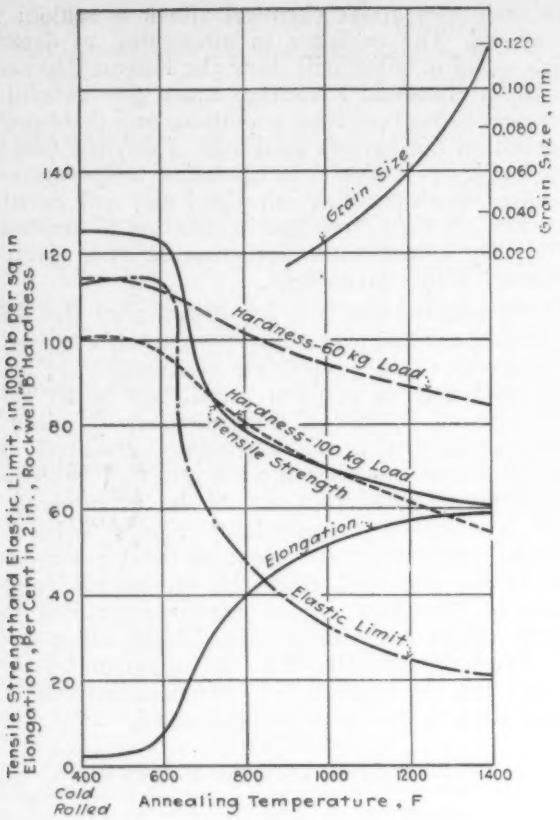

FIGURE 4

Physical properties of copper-silicon alloy sheet. (Type A, cold-rolled 67 percent, annealed as indicated.)

where copper would be satisfactory the copper-silicon alloys would be equally satisfactory, and that where copper would be unsatisfactory there is little probability that the copper-silicon alloys would be otherwise.

Those particular aspects of design, construction, and operation which in respect to corrosion influence the performance of copper in service will in like manner influence the performance of the copper-silicon alloys. While, therefore, from the point of view of corrosion it would appear unnecessary to consider the copper-silicon alloys in separate detail, it is of definite importance to consider the characteristic physical and mechanical qualities of these materials in so far as they affect their application to the construction of corrosion-resisting equipment.

Table 3 and Figure 4 present data on the physical properties of a typical copper-silicon alloy. This table does not refer to the product of any particular manufacturer, but is intended to be representative of this entire class of product. While the corrosion-resisting properties of copper have been retained in the copper-silicon alloys and excellent physical properties introduced, it will be noted from an inspection of this table that the high thermal and electrical conductivities characteristic of copper have been drastically reduced and are, together with the strength of the alloy, comparable to mild steel. The reduction of the thermal conductivity is of considerable significance in connection with these alloys, as it is a large factor in rendering them easily welded, either with the gas torch, the electric arc, or by resistance methods. Welded joints so obtained are substantially autogenous in character and introduce none of the corrosion problems which are so frequently incidental to the use of soldered or brazed joints.

There are many industrial applications in which welded copper-silicon alloy constructions are superseding, with substantial economy, steel constructions lined or covered with copper or other corrosion-resistant material. The economy inherent in this new type of construction may not always be apparent from a comparison of first costs, but is readily discerned when the maintenance costs of lined equipment are taken into consideration.

There are many other fields of application in which the use of copper-silicon alloys in the form of structural members such as bolts, screws, tie rods, etc., will reduce maintenance and replacement costs to an extent which will more than justify an initial higher material cost. In the past, the use of brasses in such applications has often proved unsatisfactory because of inadequate strength and inadequate resistance to corrosion.

The references to these alloys in the literature are relatively few because of their comparatively recent commercial development. However, the fabricating companies manufacturing these alloys have individually compiled and published information with reference to the properties of their particular products and the methods of welding and otherwise fabricating them.

TIN BRONZES AND ALUMINUM BRONZES

The tin bronzes, or, as they are commonly called, the phosphor bronzes because of the practice of using phosphorus as a deoxidant in connection with their manufacture, are of some engineering interest. They possess excellent corrosion-resisting properties, which in general are comparable to those of copper and the copper-silicon alloys. However, because of the relatively high cost of the tin entering into their composition and the expensive nature of the fabricating operations necessary to the production of mill products made of them, they are not used extensively in the wrought form as materials of construction.

One of the principal applications of the wrought tin bronzes in the construction of corrosion-resisting equipment is for use as welding rod for the purpose of electrically welding copper sheet. The welds so obtained, while not autogenous in character, nevertheless are very satisfactory with respect to strength and appear adequate in most applications in so far as corrosion resistance is concerned. Tin bronzes also are commonly used in the fabrication of such parts as valve seats, springs, and similar small parts, where good corrosion resistance is desirable (35, 48, 67, 80, 81, 83-88 inclusive). The high cost of these alloys, however, prevents their widespread application in sheet and other structural forms.

Aluminum bronzes, also, are used to some extent in wrought form, and they also possess high strength and other excellent physical properties. Ordinarily, the amount of aluminum in the commercial wrought forms does not exceed 10 percent.

In general, the aluminum bronzes, from the standpoint of corrosion, are characterized by excellent resistance to the corrosive attack of acid solutions, and in this respect not only are generally superior to the brasses but, under some conditions, superior to copper and the copper-silicon alloys (28, 89, 90). Under certain conditions, however, it would appear that aluminum bronzes having amounts of aluminum in

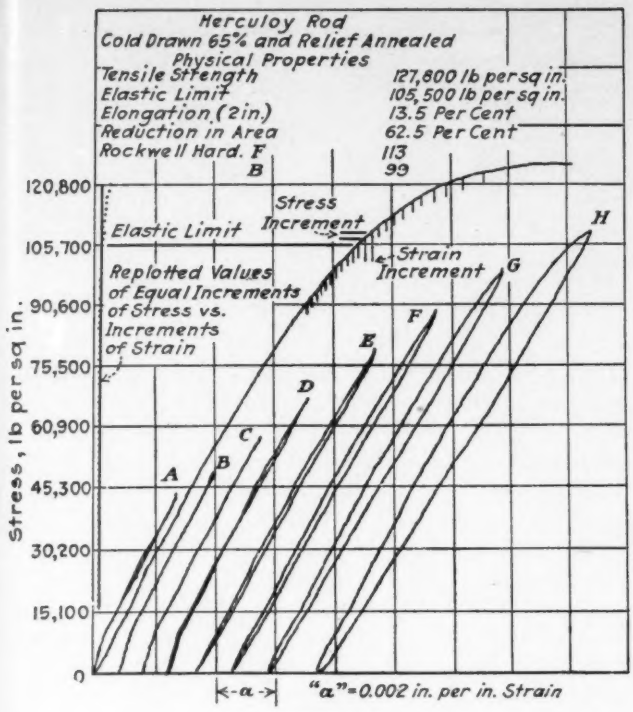

FIGURE 5

Elasticity Characteristics, Copper-Silicon Alloy.

(Curve A, 45,000 lbs. per sq. in.; B, 50,000; C, 60,000; D, 70,000; E, 80,000; F, 90,000; G, 100,000; H, 110,000. Sample loaded to these stresses and loads released in order listed. A second sample was used for the stress-strain curve and elastic-limit determination. Each curve has its own zero point.)

excess of about 7 or 8 percent are subject to a type of corrosion analogous to dezincification as mentioned in connection with copper-zinc alloys. Here also there would appear to occur a primary solution of the alloy followed by deposition of spongy copper by displacement (91).

The aluminum bronzes in the wrought form are ordinarily supplied as tubes and rods and seldom as sheets. Their properties in these forms frequently are modified by the addition of small percentages of nickel (81).

In general, the application of wrought aluminum bronzes in the construction of corrosion-resisting equipment is limited by two factors. The first is that wrought forms of these alloys present manufacturing difficulties which tend to increase their cost, and the second is that improper control of the manufacturing operations may introduce causes of failure of the product under exposure to corrosive conditions. These factors particularly render wide sheet metal of this alloy very expensive and generally unavailable as a commercial product. Still further, the aluminum bronzes are handicapped in respect to their industrial applications by the difficulties they offer to successful welding.

From the point of view of corrosion resistance, the field of application of the wrought aluminum bronzes of the most interest at present appears to be the condenser-tube field, in which they have been recently used with some indications of success. However, experience with them for such use is not yet sufficiently extensive to warrant the drawing of definite conclusions as to their actual value in that type of application.

CUPRONICKELS AND NICKEL SILVERS

The alloys of copper and nickel, commonly termed "cupronickels," have found extensive application in the engineering fields in the form of condenser and heat-exchanger tubes. The trend toward the adoption of cupronickel in such applications has been increasingly marked as the design and operation of land and marine power stations has introduced factors leading to an increasingly severe corrosive action on the condenser tubes.

The most common of these tube alloys are those containing 80 percent copper and 20 percent nickel, and 70 percent copper and 30 percent nickel. Each of these has excellent physical and chemical properties. In this connection the reader is referred to Table 4 which lists the general physical characteristics of the standard cupronickel condenser-tube alloys, including those containing zinc.

There has been a considerable use of cupronickel tubes which have been modified as to properties by the inclusion in the alloy of zinc in amounts up to 5 and 6 percent. While the imparting of a beneficial effect in respect to resistance to corrosion by the inclusion of zinc is somewhat open to question, there is no persuasive evidence that any notably deleterious effect is caused by so modifying the alloy.

Characteristically, the cupronickels are notably resistant to general chemical attack, impingement attack, and erosion. Where operating conditions are particular severe, the desirable characteristics of the 70/30 cupronickel condenser tubes are leading to its extensive use.

While it is true that the aluminum brasses, in respect to their ability to withstand impingement corrosion, closely approximate cupronickel and are less costly, cupronickel nevertheless offers outstanding advantages when compared with aluminum brasses as more severe operating conditions are encountered. When impingement corrosion or erosion alone are to be considered, aluminum brass might constitute a sound economic engineering choice, but where chemical action is accelerated by operating temperatures

TABLE 4

Physical Properties of the Copper-Nickel Alloys

MATERIAL	Tensile Strength, Lbs. per Sq. In.		Elastic Limit, Lbs. per Sq. In.		Elongation, Percent		Rockwell B Hardness		Melting Point, C	Density, Lbs. per Cu. In.	Coefficient of Expansion	Electrical Conductivity[1]	Thermal Conductivity[2]	Modulus of Elasticity, Lbs. per Sq. In.
	Hard	Soft	Hard	Soft	Hard	Soft	Hard	Soft						
Cupronickel (80 Cu, 20 Ni)	80,000	49,000	75,000	18,000	3	42	87	21	1200	0.321	0.0000159	6.47	0.087	17.0
Cupronickel (70 Cu, 30 Ni)	84,000	49,000	80,000	18,000	4	50	87	23	1220	0.323	0.0000162	4.75	0.093	17.0
20 Percent nickel silver (70 Cu, 10 Zn, 20 Ni)	81,000	49,500	78,000	16,500	5	44	86	12	1150	0.321	0.0000164	4.8	0.069	18.0
18 Percent nickel silver (64 Cu, 18 Ni, 18 Zn)	100,000	54,500	80,000	18,000	5.5	42	94.5	40	1110	0.316	.....	5.91	0.080	18.0
10 Percent nickel silver (65 Cu, 25 Zn, 10 Ni)	90,000	50,000	75,000	18,000	3	45	90	52	1010	0.313	.....	8.27	0.110	17.5

Data based on information published by Revere Copper and Brass, Inc., American Brass Company, and Chase Brass and Copper Company.
[1] Percent of International Annealed Copper Standard.
[2] Cal. per sq cm per cm per sec per C at 20 C.

in excess of 100° F., the aluminum brasses can, and on occasion do, fail rapidly.

For these reasons the cupronickels are being increasingly applied in the form of heat-exchanger tubes in the oil and other processing industries, in cases where operating and tube-wall temperatures are sufficiently high to cause rapid deterioration of Admiralty, aluminum brass, and similar modified brass tubes.

Cupronickel in the form of sheet and strip has not as yet been extensively applied in the construction of industrial equipment. However, the use of cupronickels in condenser tubes, and the uniformly excellent results obtained with them, has called attention to their excellent properties as corrosion-resisting metals, and, therefore, it is only reasonable to expect that the use of these alloys in sheet and other structural forms will increase (14, 20, 21, 81, 92-96 inclusive).

CASTING ALLOYS

So far this discussion has been confined, in respect to alloys, almost exclusively to those which are susceptible of mill production in wrought form, such as sheet, strip, tube, rod, wire, and shapes. While most of these alloys are of particular interest in the wrought form, many of them nevertheless can also be used in the form of castings. Many of the popular casting alloys, on the other hand, cannot be commercially fabricated into wrought forms by either hot- or cold-working.

The engineer in selecting an alloy for a corrosion-resistant casting obviously must, as his primary concern, consider the corrosion resistance of available casting alloys, and then give his attention to the mechanical and economic factors involved, such as the strength of the alloys in the cast form, their machinability, cost, etc. The range of alloy composition, however, is not limited in the case of a casting by the necessity of insuring that the composition be such as will permit mill fabrication of the alloy selected.

Brass castings are extensively used for valve bodies, pipe fittings, and similar products where only the normal corrosive attack of industrial and domestic waters and similar substances are anticipated. In this type of application we find an alloy commonly known as "85-5-5-5," widely used and giving satisfactory results in its usual applications. However, when corrosion problems become more severe than those just mentioned, or higher strengths are required, as is illustrated by the application of castings to pickle-tub racks and similar articles, there is an extensive use of the aluminum bronzes. With cast aluminum bronze, high strengths and high resistances to direct chemical attack are secured, and these properties generally are superior to those offered by copper, or the silicon-copper alloys, or the common brasses.

TABLE 6

Physical Properties of Typical Cast Bronzes

COMPOSITION	Tensile Strength, Lbs. per Sq. In.	Elastic Limit, Lbs. per Sq. In.	Elongation, Percent	Red. Area, Percent
Aluminum bronze—				
(Cu, Al 0.9, Fe 1.25)	75,000	20,000	30	35
(Cu 88, Al 10, Fe 2)	75,000	30,000	18	18
Gun metal—				
(Cu 88, Sn 10, Zn 2)	30,000–45,000	11,000–14,000	15–40	..
(Cu 88, Sn 8, Zn 4)				
Eighty-five three fives—				
(Cu 85, Sn 5, Zn 5, Pb 5)	30,000	10,000	15	..

In general, it may safely be said that there is a wide permissible range of composition in the copper-base casting alloys. Necessity, and, it would seem, even personal whims, govern the composition of many copper-base alloys used in practice, and it would serve no useful purpose to attempt in this paper to enumerate all of the many variations which are to be encountered, or their physical and chemical properties. Table 5 gives the composition of certain widely used copper-base alloys and the rates at which they are attacked by certain reagents commonly encountered in the oil industry. Table 6 lists the physical properties of the more important of these alloys (35, 61, 104, 105). Test conditions are given in Table 7.

As a further generality, it may be stated that the chemical characteristics of the copper-base casting alloys are qualitatively similar to those of the corresponding wrought alloys previously discussed. Because of a wider latitude in composition, the cast alloys may present quantitative variations from the properties of the wrought alloys, but the corrosion data previously submitted will, it is believed, serve as an adequate guide in respect to corrosion resistance in any consideration of copper-alloy castings.

DESIGN AND MECHANICAL FACTORS

It is, of course, obvious that the designing engineer should have a full comprehension of the physical and mechanical characteristics of his materials of construction as well as a knowledge of their chem-

TABLE 5

Corrosion Data—Cast and Wrought Bronzes—Rates Expressed as Penetration in Inches Per Year, Ref. (79)

TEST No.	1	2	3	4	5	6	7	10	10A	11	12	13	14	15
Cast bronze (80 Cu, 8 Zn, 4 Sn, 8 Pb)	0.0006	0.0026	0.0017	0.0001	0.0037	0.0113	0.0586	.....	.....	0.0003	. . .	0.0138	.....	.....
Cast bronze (acid metal) (85.5 Cu, 10.5 Sn, 4 Pb)	0.0006	0.0040	0.0017	nil	0.0127	0.0112	100%	0.0463	0.0109	.....	.....	.....	.....	.....
Valve metal (86 Cu, 4 Zn, 7 Sn, 3 Pb)	0.0013	0.0028	0.0017	nil	0.0090	0.0347	0.1059	.....	.....	.....	.....	.....	0.0037	.....
Bronze (88 Cu, 12 Sn)	0.0006	0.0024	0.0023	nil	.....	0.0024	0.0941	0.0397	0.0129	0.0001	0.0001	0.0065	0.0036	.....
Cast bronze (88 Cu, 10 Sn, 2 Pb)	0.0018	0.0021	0.0025	nil	0.0167	0.0214	100%	.....	.....	0.0011	0.0008	0.0135	.....	0.0004
Bronze (88 Cu, 2 Zn, 10 Sn)	0.0003	0.0003	0.0016	nil	0.0056	0.0033	0.0703	.....	.....	0.0005	0.0002	0.0095	.....	0.0078
Bronze (77 Cu, 8 Sn, 15 Pb)	nil	0.0037	0.0028	0.0002	0.0084	0.0193	100%	0.1435	0.0098	0.0006	0.0005	0.0157	0.0024	.....
Aluminum bronze (90 Cu, 10 Al)	.....	.....	0.0012	.....	0.0031	0.0189	0.0585	.....	.....	.....	.....	.....	.....	.....
Aluminum bronze (cold-rolled) (88-96 Cu, 2-10 Al, FE)	0.0004	0.0015	0.0015	nil	0.0100	0.0320	0.0883	0.0586	0.0057	.....	.....	.....	0.0033	.....
Aluminum bronze (hot roll) (94 Cu, 6 Al)	0.0013	0.0020	0.0013	nil	0.0078	0.0298	0.0919	.....	.....	0.0001	0.0001	0.0067	.....	.....
Aluminum bronze (89 Cu, 10 Al, 1 Fe)	0.0002	.....	0.0011	nil	0.0183	0.0096	0.0376	.....	.....	.....	.....	.....	.....	.....

For test conditions see Table 7.

TABLE 7

Corrosive Conditions for Tables 5 and 6, Ref. (79)

Test No.	SERVICE	Temperature or Pressure	Period of Tests	REMARKS
1	Fresh water	100–120 F	186 days	Open condenser, no O_2
2	Salt water	100–120 F	164 days	Open condenser, no O_2
3	Salt water	100–120 F	149 days	pH 8.5, NaCl 4–4.5 g per liter
4	Steam	150 lb. per sq. in.	206 days	Steam trap, vapor
5	Crude-oil vapor	Atm temp	195 and 175 days	Light West-Texas crude, agents—O_2, H_2O, H_2S
6	Naphtha	Atm temp	125 days	Agents—H_2S, H_2O, HCl
7	Naphtha-vapor cracking-coil bubble tower	350 F, 90 lb. per sq. in.	136 days	Agents— H_2S, mercaptans, naphthenic acids
10	HCl, 5 percent	Room temp	24 hours	HCl for cleaning
10A	HCl, 5 percent with acid sludge 3 percent	Room temp	24 hours	HCl for cleaning and sludge for inhibitor
11	Caustic soda (lab. tests without agitation)	Room temp	50 days	NaOH 468 gr per liter—Na_2S 17.6 per liter
12	Caustic soda (lab. tests without agitation)	Room temp	60 days	NaOH 155 gr per liter—Na_2S 28 gr per liter
13	Acid wash water	Atm temp	75 days	Agents—SO_2, NaCl, SO_3
14	Separated water from crude naphtha	.....	64 days	H_2O pH 4.0; HCl, H_2S
15	Rerun naphtha	100 F	21 days	pH about 3, small amounts H_2S and SO_2

ical properties when designing corrosion-resisting structures and equipment.

In this connection it is often overlooked that cuprous materials do not have a "yield point" in the sense in which that phrase is used in connection with ferrous materials, and that, therefore, where yield strengths, or yield points, are given for cuprous materials, such values are really only expressions of a property that by custom is assumed to exist, but which in fact has no real existence. The value of the assumed property of the yield point of a cuprous material is only an approximation of the value of its elastic limit. It is, therefore, recommended that the designer in working with copper alloys, base his design on the existent property of elastic limit.

The value of the elastic limit of a cuprous material may be determined by the method illustrated in Figure 6. Briefly, that method consists in plotting from the stress-strain curve equal increments of stress against corresponding increments of strain. The point at which the graph so obtained shows a marked change in slope is for all practical purposes the elastic limit of the material. The soundness of this method is indicated by Figure 5, in which is included load-unload curves showing that specimens of material loaded to below, and up to, the value of the elastic limit so determined, have no permanent set when the load is released, while specimens loaded in excess of that value have a permanent set upon release of the load. It is felt that values of elastic limit so determined have a real significance for purposes of mechanical design and that the use of such values is to be preferred to the use of the more or less fictitious yield strengths arrived at by arbitrary definition (106-109 inclusive).

In addition to considering the basic physical and chemical properties of a corrosion-resisting material, the engineer must take cognizance of the characteristics of that material when in the particular structural form in which it is to be used. An alloy bar, for example, or a tube or sheet possess certain characteristics which are imparted to it by the fabricating operations to which it has been subjected and which in many instances exercise a profound influence on its ability to stand up satisfactorily under corrosive attack.

Copper-base alloys are seldom susceptible of hardening and strengthening through heat-treatment, and in most industrial forms these alloys are tempered by cold-working. In certain of these alloys, notably the brasses, the aluminum-bronzes and the silicon-copper alloys, excessive stresses, residual in the metal as a result of cold-working, are likely to lead, under the influence of even mild corrosive attack, to stress-corrosion cracking, with resulting rapid failure of the part in question. Structural forms of these alloys, to insure against such failure, should be relieved of residual stresses by so-called "relief annealing," that is to say, heat-treatment below the recrystallization (or softening) temperature, whenever such treatment is possible.

In the construction of corrosion-resisting equipment, relief-annealed material should be used, and when additional severe cold-working is an incident to construction, adequate steps should be taken to relieve the member of any excessive stresses that may have been introduced by such cold-working. In ordering products made of the modified brasses, such as Naval brass, manganese bronze, and similar alloys, the engineer should avoid specifying physical properties which represent maxima attainable only through extreme cold-working of such alloys. It is seldom possible to retain such maxima in adequately relief-annealed products. Attempts to utilize such products in the extreme hard-worked condition are likely to result in failures having their origin in stress-corrosion cracking (90, 106, 110, 111, 112).

It is also pointed out in the foregoing connections that hard-drawn copper-base alloys are peculiarly sensitive to the so-called "notch effect" in so far as fatigue resistance is concerned, and that this sensitivity is drastically reduced by relief annealing.

Where corrosion fatigue presents a possible source of failure, it should be remembered that in general the hot-rolled non-ferrous alloys have a much higher endurance limit in fatigue than the same alloys produced by extrusion methods. Thus, hot rolling should be specified as the method of fabricating such alloys whenever a maximum resistance to fatigue is desired and the alloys are of such nature that it is possible to fabricate them by such method (107).

The mechanical design of a structure often determines its ability to withstand corrosion. Problems in design, if improperly handled, may result in rapid failure of a structure, under conditions of corrosion, that otherwise would, if the design were properly handled, give long and satisfactory service.

Failures of this kind are, of course, not peculiar to copper and the copper-base alloys, and the precautions in design necessary to be observed in connection with constructions employing copper and its alloys are in general the same as those which must be observed in connection with the employment of other structural corrosion-resisting materials.

It is widely recognized that dissimilar metals in contact are a frequent source of destructive corrosion. Failure of this type may result when copper, as a sheathing or lining material, is joined by soft-

soldering. Soldered joints are often the foci of corrosive attack and pitting, and line corrosion of the copper adjacent to the joint can and does in many cases cause failure (90). In general, in the case of roofing and similar applications of sheet copper, it is recommended that the presence of soldered joints be reduced to a minimum, and that, so far as used, care be taken in the selection of soldering fluxes, and highly acid fluxes be avoided (107, 113).

In tank constructions employing sheet copper, various possible methods of joining the sheets are presented. Riveting, frequently in combination with soft-soldering, or brazing with hard solders, such as high zinc-copper alloys, is a method frequently employed. Other frequently utilized methods are brazing with materials of the naval-brass type and brazing or welding with the phosphor bronzes or the silicon-copper alloys.

It is also possible to obtain joints that are substantially autogenous in character through brazing with certain silver-copper alloys and copper of high phosphorous content.

The engineer should give careful attention to the joining method adopted, with particular reference to the chemical activity at the joint that might be anticipated in the handling of a specific material.

Further, with reference to tanks and the like, it should be observed that one of the advantages orfered by the silicon-copper alloys is that they can be so readily fabricated by autogenous welding, with the consequent elimination of corrosion problems incidental to the presence of dissimilar metals in contact.

With copper, as with any other sheathing or lining material, the lack of proper provision for expansion and contraction of the metal with temperature changes can lead to cracking and other forms of corrosion-fatigue failure. Adequate provision for such expansion and contraction should be made, particularly in the design of structures utilizing extended areas of copper as a sheathing or lining material, and particularly in the case of copper roofing.

It is true of copper and its alloys, as it is true of other corrosion-resisting materials, that impingement corrosion will frequently cause failure in cases where the material of construction is otherwise ordinarily immune to the action of the corrosive material involved. The structural design should be so controlled, when possible, as to eliminate impingement attack entirely, or to reduce it to a minimum. When impingement corrosion is anticipated, protection or reinforcement should be incorporated in the design to avoid, so far as possible, the consequence of this effect.

There is probably no field of use where impingement is such a factor in determining the ultimate life of the material as in the condenser tube (114). It is to their excellent ability to resist impingement attack that the cupronickels and the aluminum brasses owe their success in the condenser-tube field.

While it is necessary in the design of corrosion-resisting structures to consider, as has been suggested, many mechanical factors that may be involved in the corrosion problem, it is also frequently necessary carefully to weigh the probable effect of minor variations in the composition of materials to be handled. For example, the literature and data referred to herein give extensive information as to the resistance to sea-water corrosion of most of the commonly available structural materials. "Sea water" is, however, a large and comprehensive term, and the corrosive nature of sea water varies considerably with the location in which it is found. Cold, north-Atlantic water, the warm waters of the tropical seas, the polluted harbor waters adjacent to industrial cities and large ports, and the brackish waters of tidal streams, all present different problems. A material which will satisfactorily withstand the corrosive attack of cold, clean, north-Atlantic water may fail quickly and completely when exposed to harbor water contaminated by industrial wastes.

A more striking illustration of the influence of minor constituents or impurities is to be found in our industrial and domestic fresh-water supplies. There are sections of the country where the water supplies are such that there is no apparent economic advantage in the use of nonferrous pipe. There are other sections of the country where the waters are of such a nature that there is a definite economic advantage in the use of brass or copper pipe. However, even in these latter cases, there is a considerable variation, and there are known water supplies where ordinary high-zinc brasses do not give adequate life and with which it is necessary to use 85/15 or red-brass pipe or else copper tube. Then, we have extreme cases where industrial and domestic water supplies are characterized by low permanent hardnesses in combination with a high CO_2 content, and such waters will attack to some degree practically every available commercial metal. In such extreme cases we find rapid destruction of some types of pipe, and a corrosive action which would constitute a hazard to health if certain other types were employed, and the water even on red brass and copper would have sufficient chemical activity to cause an objectionable green staining of plumbing fixtures and at times a slight discoloration of the water. In such extreme cases tinned-copper tubing is recommended (115, 116).

The foregoing instances are cited primarily to illustrate the necessity of considering factors which at first glance might appear to be unimportant, but which, as a matter of fact, may constitute the direct cause of corrosion failure and unsatisfactory service if their probable effect is not anticipated by the engineer.

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Tube door platform of 750-pound cracking coil. Coil setting and towers of another unit in the background. Standard Oil Company of New Jersey, Bayway refinery.

Solvent Refining . . . A Study of Its Molecular Physics

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PART I

Theory and Its Experimental Basis

IN principle, solvent refining of oils is a technical application of two of the oldest "chemical" operations: extraction and precipitation. It will be well, however, to remember that in general these chemical operations may involve (1) changes of phase and (2) of substance, i. e., chemical reactions, at least as transitory stages. Conversely, solvent refining involves certain operations with comparatively inert compounds in liquid phases, with the purpose of avoiding chemical reactions and subsequent costly recovery operations. Thus, while chemical reactions are characterized by a mutual interchange of electrons, the processes of solution and precipitation involved in solvent refining have a different basis, being confined to the temporary electrostatic interaction of the electron systems of neighboring molecules.

This interaction is known as solvation and association, and while there is as yet no absolutely exact discrimination possible between these phenomena and the formation of intermolecular compounds, the modern better understanding of the origin of such molecular interaction makes it possible to go beyond the old chemical statement that "similar substances dissolve each other."

We know from experiment and from the nature of the molecular forces that the liquid state can no longer be regarded merely as a more condensed state but that this greater condensation results in the formation of molecular complexes representing states of order. The nature and the formation of these states depends on the strength and distribution of the molecular forces of the molecules which are closely related to the shape of the molecules. The thermodynamic laws of solution are consequences of molecular structure and forces. From the standpoint of our present knowledge the questions of solubility are inseparable from these states of order which are characteristic for liquids.

A study of solvent refining has to start with the molecular forces which determine the liquid state and the underlying characteristics of electronic systems: their polarizability and its dissymmetry and the dissymmetry of electronic distribution with its resulting molecular polarity. The former results in the production by electric fields of temporary electric moments within the molecular structures, while the latter constitutes the permanent (= dipole) moments. The fundamental characteristics of electronic structures leading to these two types of electric moments were briefly outlined in an earlier paper in this journal, and it was shown how these moments give rise to the molecular forces.[1]

Dr. S. Kyropoulos, author of the present series of two articles on solvent refining will be remembered as the contributor of that important series of three articles dealing with "Oiliness, Its Meaning and Value in Motor Oils," which appeared in THE REFINER *last year.*

Dr. Kyropoulos, now doing special work at the California Institute of Technology, Pasadena, California, where he has been located since the first of the year, was formerly Professor of Physical Technology, in the University of Goettingen, Goettingen, Germany.

In the solutions under consideration, the oils or their distillates, the various types of compounds are held in solution as solvation complexes by the mutual interaction of the molecular forces. Solvent refining, or more precisely, solvent extraction, means the controlled breaking up of these solvation complexes and the substitution of one partner (or one type of partner) of the solvation complexes by another which has, moreover, so slight a tendency to form solvation complexes with the displaced partner that a second layer is formed, composed practically exclusively of the refining addition and the new solvation complexes.

The object of our study is to correlate molecular structure in terms of polarizabilities and permanent electric moments with the molecular forces arising from them and with its characteristics of solvate formation.

As a result it appears that there is much material, originally collected for purely scientific purposes, available as a basis for deeper insight into solvent refining processes and for their scientific investigation.

EXPERIMENTS AND THEIR THEORETICAL EVALUATION

It might be inferred that molecular structure is primarily a chemical problem, that physics contributed comparatively little to its elucidation, and that such contribution often bears rather the character of

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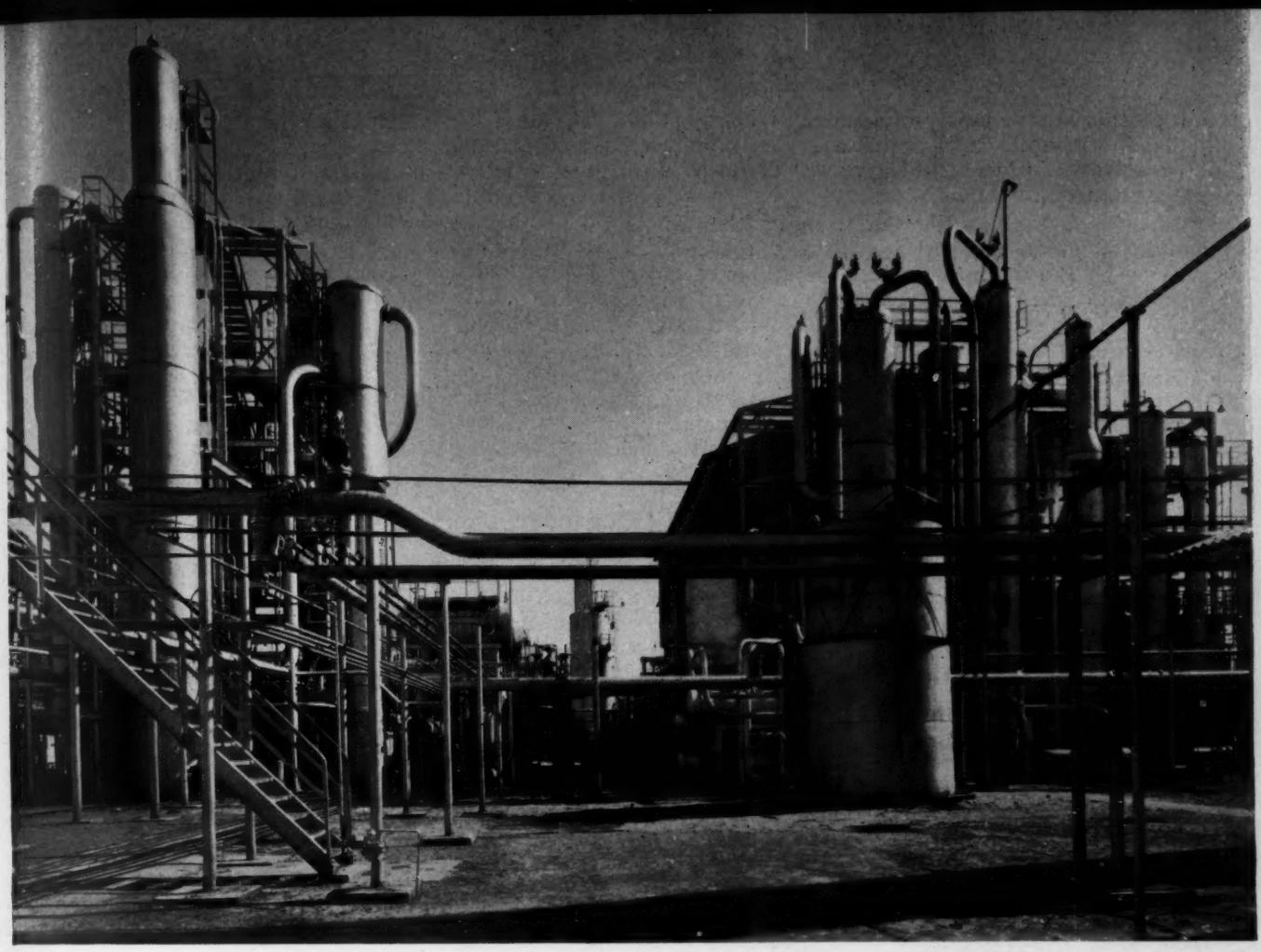
confirmation of results already gained with chemical methods. The adoption of this point of view neglects the essential point of the problem, which does not consist in the study of any chemical reactions but in the study of those factors of chemical constitution which bring about the more transitory combinations of molecules which are not a problem of chemistry but of molecular forces. For the basic experimental facts underlying the phenomena of polarizability and bond moment and the various kinds of molecular forces the article quoted above[1] should be consulted along with the literature cited there.

The classical example, known to the chemist, for many years, of non-chemical interaction in liquids is dipole association. It has been studied best with compounds containing the OH- and COOH-group. These are, with the exception of water, mainly the alcohols and fatty acids. For convenience we limit ourselves to the derivatives of the paraffins. A convenient method for the study of dipole association is the measurement of the dipole moment (or bond moment C-OH, C-COOH) in varying concentrations of these compounds in hexane or benzene. The variation of this moment with concentration shows that various sorts of complexes are formed which are in the cases of the acids so strongly bound that even in the most dilute solutions dimolecular complexes prevail[2]. The first step of association, the formation of double molecules by dipole association, is followed by the formation of higher complexes between the double molecules. The forces between the doublets, U, increase with increasing chain length showing (see 1a, sections 6 and 7) the characteristics of the induction and dispersion forces. The decrease of the heat of dissociation of the doublets (Q) with increasing chain length shows (1) that it is not the induction and dispersion forces which become effective in the first step of association of the molecules, but the dipole (or alignment) effect of the polar groups; (2) that there is a steric effect, a decreasing accessibility of the polar group with increasing chain length. A comparison of the n-butyl alcohol with the branched tertiary butyl alcohol shows that the screening effect of the branched group is appreciably the same.[3]

On dealing with solubility phenomena the polarizing effects of polar bonds (even of molecules with resulting moment zero: C Cl_4) on neighboring atoms have to be considered. This effect is demonstrated best in those cases where it occurs within the molecule. We recall from the previous article[1] that the dipole moment of a molecule may be calculated by vector addition of the individual bond moments. Thus, with p-dichlorobenzene the moment is found to be zero both by measurement and calculation. For m-dichlorobenzene the measured value is 1.48×10^{-18} and the calculated 1.55×10^{-18}, showing a slight difference[4]. This difference is much greater with the ortho-compound, where the measured value is 2.25, the calculated 2.67. This "ortho-effect"[5] arises from the mutual polarization of the Cl-C-moments, leading, besides, to a higher degree of saturation of the field of force of this part of the molecule. In general, this polarization-effect with its influence on the magnitude and "saturation" of the resulting moment and consequently on the association characteristics of a compound may bring about very different solvent power with similar compounds. The polarization-effect was studied by Smyth and Dornte[3-6] in the case of paraffin halides and alcohols and by Stuart[7]

Pilot plant for solvent treating. Edeleanu Laboratories.



Benzol Acetone Dewaxing Plant and Furfural Refining Plant, Magnolia Petroleum Company, Beaumont, Texas. Designed and erected by The Lummus Company.

for nitriles, halides, alcohols and ethers and generally for the value of the moment in homologous series which should be constant where there occur no such differences in polarization. Practically, the influence does not go beyond the C-atom adjacent to the polar bond, for example, the C-Cl bond, and is of course greater in a tertiary compound.

From this necessarily incomplete collection of facts we may draw several conclusions for an approach to a systematic theory of solvent refining:

In general, solvent extraction will be the result of the competition of molecular forces between the molecules of the solvent A and the molecules of the oil B.

(1) So far as non-polar solvents are concerned (e. g., propane) the chain length or a similar factor, representative of the possibility of close atomic contact and of the strength of the forces between the molecules, i. e., the polarizability, will be of outstanding importance. Their action will be determined by the induction and dispersion effect. The temperature coefficient of solvent action will bear in this case the characteristics of the temperature dependency of both of these kinds of forces, i. e.: the temperature effect will be essentially a density effect and a comparatively strong influence of external pressure is to be expected. Thus, any disadvantages of the use of higher temperatures may be compensated by applying higher pressures.

(2) So far as polar solvents are concerned, as in the majority of cases, we are (a) not concerned with the individual polar groups of the single molecule and their electric moments but with the molecular complexes resulting from the combination of the single molecules by dipole association. (b) Which combination becomes effective will depend on the characteristics of the polar group and its field of force (COOH, OH, O, NO_2, etc.); on its position within the molecule: chain length, branching of the chain, valency angles (e. g., in ether of the O-atom), i. e., the degree of screening of the moment, on its polarizing characteristics and on the very marked temperature effect upon the dipole alignment effect.

From what was said above on the competition of molecular forces in the process of solution, it follows that polar compounds with large and feebly screened moments will tend to form big and stable clusters. Thus the tendency toward solvate formation will be weak, except in the case where the foreign molecules are very strongly charged as in the case of ions in water. In general, the tendency to form solvates will increase with rising temperature with these sort of molecules because dipole association diminishes with increasing temperature.

Thus, both in case (1) and (2), dispersion and induction forces are the forces directly effective in solvate formation. The polar groups of the solvent serve (a) as a means to increase the induction effect; (b) the effect of temperature on dipole association affords a means of controlling the actually effective complexes by controlling their composition and at the same time their polarizing properties.

SOLVATION AND POLARIZABILITY

Although it is obvious that the mechanism of dipole association[8] is important from the point of

view of this study, most solvents used being polar liquids, the complexes of which are partly split up in the solvation process, this process in itself is of greater immediate importance.

A specimen case is the variation of the dipole moment of polar molecules with the solvent, as measured by the method of dilute solutions of polar molecules in non-polar solvents.[9] In some of these cases we are faced with considerable induction and dispersion effects, i. e., the polarizability and polarizing properties of the solvent influence the measured moment. Thus: hexane, cyclohexane, dekaline as solvents show little influence, their partial moments being slight, their resulting moments zero and their polarizabilities (α) small. This means that their power of dissociating the dipole complexes and forming solvates is small. The case of benzene shall be dealt with separately in a later section. In general, the influence of the solvent will be greater when the polar molecules are very small and their moments large and exposed because the induction effect of the dipoles upon the solvent molecules will be greater. The reverse will be the case where the dipole association is very strong and the dipoles are themselves strongly screened by attached chains: OH and COOH groups in paraffin-derivatives. The influence on the moment by solvation will be considerable where the solvent has a high value of α or strong group (= partial) moments: CCl_4, containing the highly polar and polarizable C-Cl bond. The influence is still greater where large group moments are far apart: p-dichlorobenzene.

As a whole, we can say that the solvent refining problem by polar solvents is a reversal of the association problem. For this reason all the vast experience collected in this field of research is immediately applicable to the study of solvent refining problems.

ANISOTROPY OF α, STRONGLY ASYMMETRIC MOLECULES AND THE STRUCTURE OF THE BENZENE NUCLEUS

The purpose of the various solvent extraction processes by polar solvents is the separation of cuts of varying "degree of paraffinicity" and we are accustomed to speak or aromatic and more or less naphthenic fractions. Here we are not concerned with any conclusions regarding the chemical constitution of oils which might be drawn from a closer study of these processes. A brief survey on this subject from a physico-chemical point of view was given elsewhere[10]; a comprehensive study is being carried on by Rossini and co-workers and by Mikeska[11]. From the point of view of the present study, solvent extraction by means of polar compounds means in general: separation according to varying degree of anisotropy of polarizability.

This anisotropy was briefly discussed in connection with molecular structure in an earlier article[12] along with the rule of Silberstein which is a convenient means of predicting the directions of the three main polarizabilities (α_1, α_2, α_{max}) within a molecule.

In the paraffin molecules the largest of the three, (α_{max}), coincides with the chain length, increasing with it to a limiting value. So far as flat or nearly flat molecules (naphthene-nuclei, benzene etc.) are concerned, the rule of Silberstein shows that α_{max} lies in the plane and again coincides with the greatest extension of the molecule. Berger[13] studied the association of non-polar compounds in non-polar solvents by means of the ebullioscopic method in conjunction with polarizability and calculated the potential of the dispersion-effect which is representative of the tendency of association between two molecules, by means of the formula of Slater and Kirkwood[14] in which the polarizability α and the number n of valence electrons of the molecule enter. A few examples will demonstrate the connection between these values and association of non-polar molecules. Thus, dekahydronaphthaline, tetrahydronaphthaline and naphthaline shows decreasing numbers of valence electrons n=58, 52 and 48 respectively and increasing α_{max} and associtaion in hexane solution in the same order. The association of these compounds decreases, however, in the same order in benzene solution, because the forces between these molecules and the benzene molecules are much stronger than between the hexane molecules, benzene being much more asymmetric with regard to its polarizability. As a whole, we see that for this reason, a greater tendency toward solvation with polar molecules is to be expected with aromatics, in accordance with refining experience.

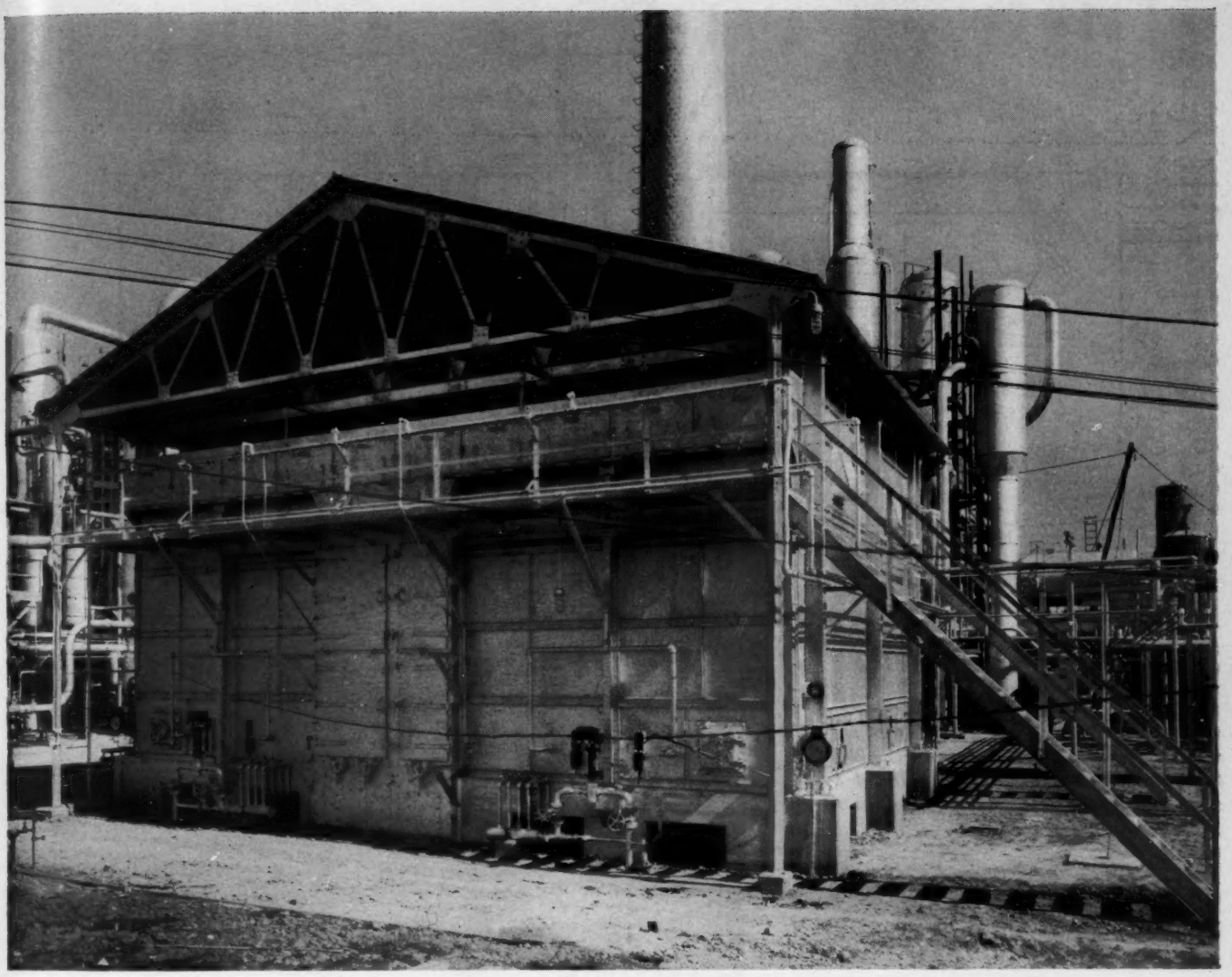
CHARACTERISTICS OF BENZENE AND RELATED STRUCTURES

The difficulties encountered by any formula in attempting to describe the physico-chemical properties of the benzene nucleus are well known. E. Huckel[15] treated this problem from the standpoint of quantum mechanics. The results are of fundamental importance for a study on solvent extraction.

Let us first briefly recall the meaning of the polarizability α and its anisotropy. The polarizability is a measure of the deformability of the outer electron cloud of an atom or a molecule under the action of an electric field. The greater α, the greater (all other factors being equal) are any induction- and dispersion-effects upon the molecule. Consequently, the potential energy of two molecules in a fixed relative position will increase with increasing α and, the greater the differences between the three main polarizabilities of the molecule, the greater will be the differences in energy between the corresponding states of mutual orientation (=association). This means, in brief, that solvent formation will be fostered by a high degree of anisotropy of α.

Both conditions: large α and large anisotropy of α are fulfilled in the benezene nucleus and some related structures.

In the first place α increases as the general atomic structure of a molecule, as a whole, becomes less densely packed. This applies to the naphthenic structure as compared with the paraffinic. Secondly, in a laminar or nearly laminar (graphite-like structure, α_{max}, lying in the plane, has rotational symmetry, which is again in favor of a mutual orientation of the molecules like a pack of cards. In the benzene nucleus, however, there are 6 free electrons out of 30 valence electrons, which do not belong to any particular bond, forming the much more loosely bound p-electron cloud. These p-electrons are much more polarizable than the rest (σ-electrons) which enter into the σ-C-C and σ-C-H bonds. These 6 p-electrons are also present in the pyridine, pyrrol, furane and thiophene rings and in other aromatics. There are 10 p-electrons in naphthaline and even in the conjugated double bond there are 4 non-rigidly localized p-electrons. In this connection we recall the fact that the -C≡C- and -C=C- bonds are much more polarizable than the -C-C- bond. Recalling, further, the considerable dissymmetry in α of the laminar benzene nucleus (the values being 123.1, 63.5 and 123.1 $\times 10^{-25}$ respectively) we recognize at



Heater for Furfural Refining Unit, Magnolia Petroleum Company, Beaumont, Texas. Designed and erected by The Lummus Company.

once why the aromatics are preferentially forming solvates with the polar solvents used in the various refining processes and why the naphthenic compounds, which have no p-electrons but still a comparatively large α_{max}, are second in order etc.

Briegleb[16] presented fundamentally valuable contributions to this point by studying the intermolecular compounds between aromatics and polar molecules. These researches throw some light on the mutual orientation of the molecules, the districts within the molecules where this form of combination takes place and on the particular molecular forces and energies involved.

The present brief study, with its inevitable lack of completeness, must be regarded rather as an attempt to correlate a vast field of modern physico-chemical research with an important industry, hitherto practically dominated by the chemist, than an attempt to present a complete theory of the subject. It appears, however, that this deficiency is due less to the matter than to our slender knowledge of the precise chemical nature of the constituents of petroleum and to the fact that, apparently, the connections presented here were not considered before on the part of oil chemists.

In Part II the properties of the most important solvents used in practice shall be briefly discussed with reference to the points of view adopted in the present paper and their application in the selection and development of solvents for refining purposes.

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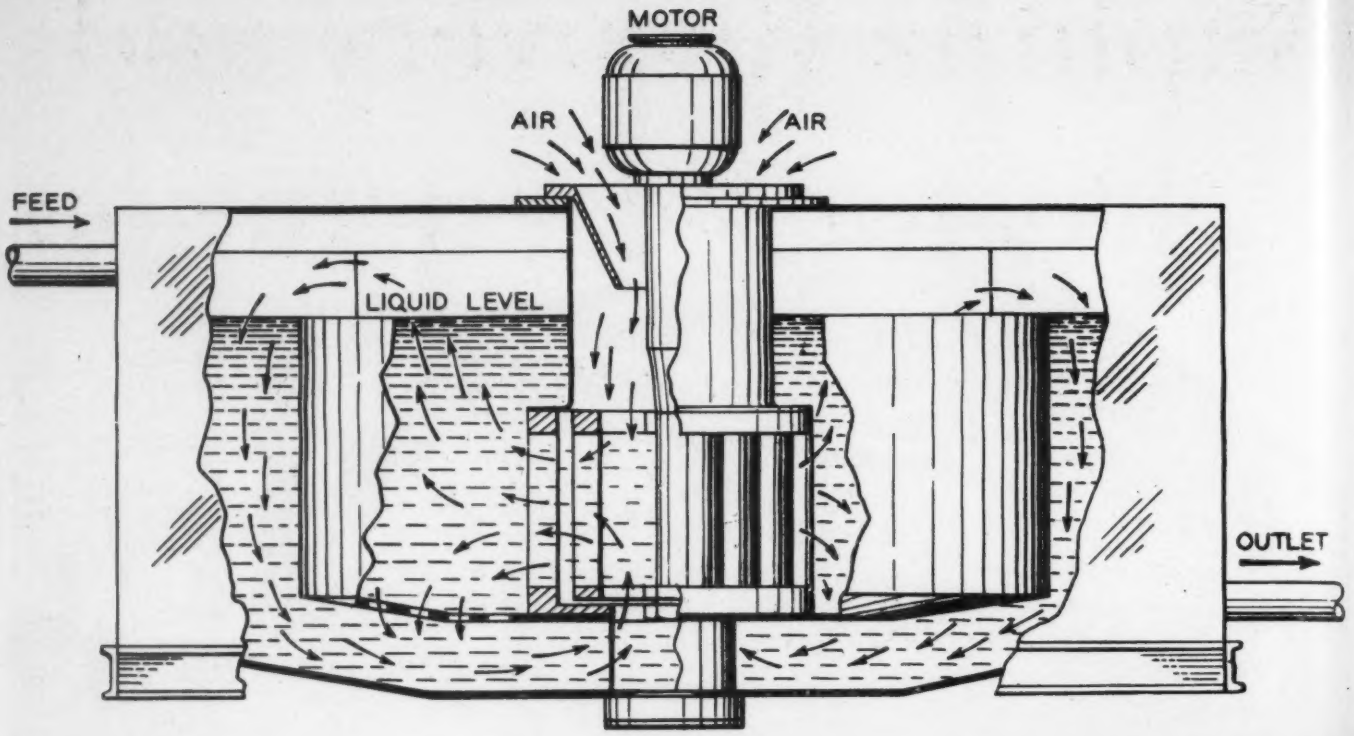
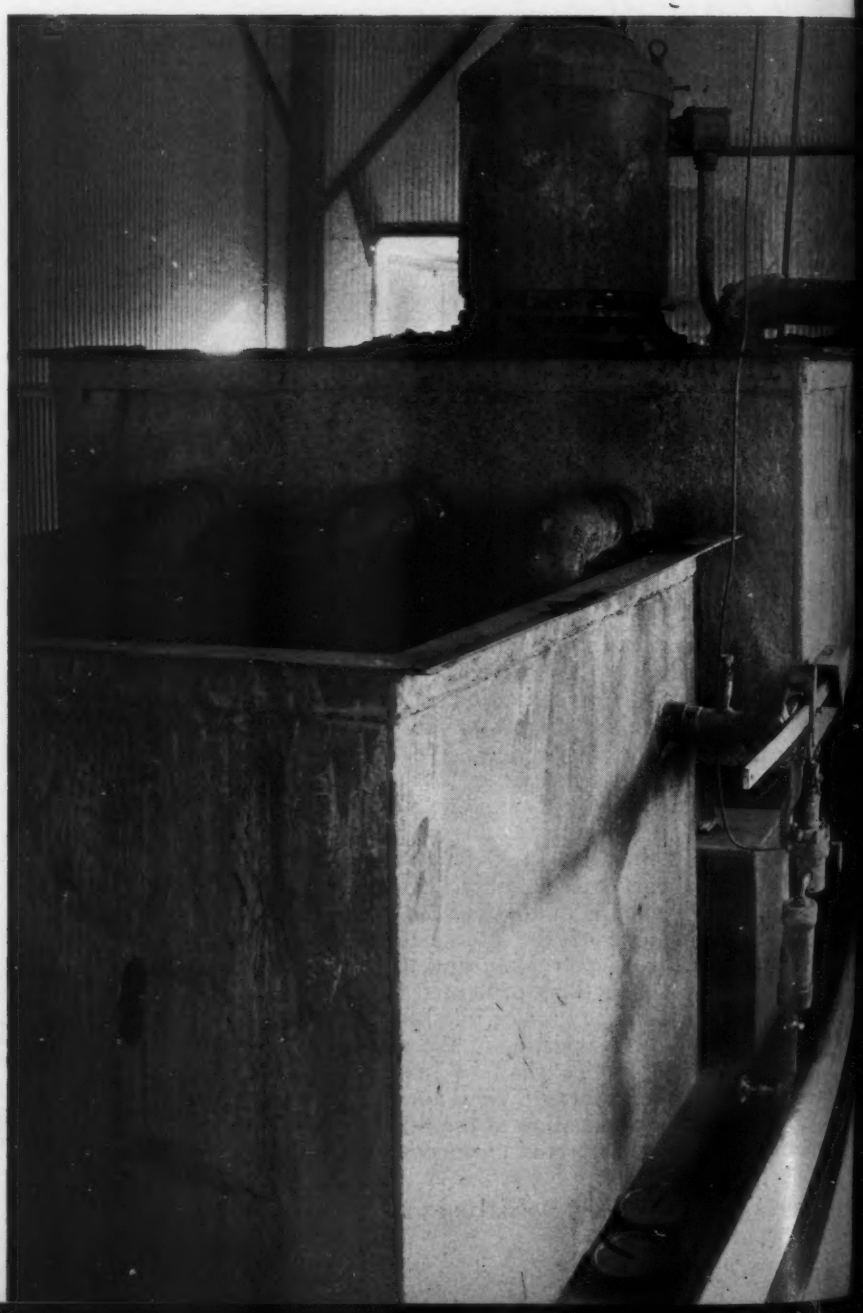


FIGURE 2

A suspended motor driven rotor surrounded by a cylindrical stator secured to the bottom of a tank and surrounded by a sleeve forms the special mechanism of the regenerator.



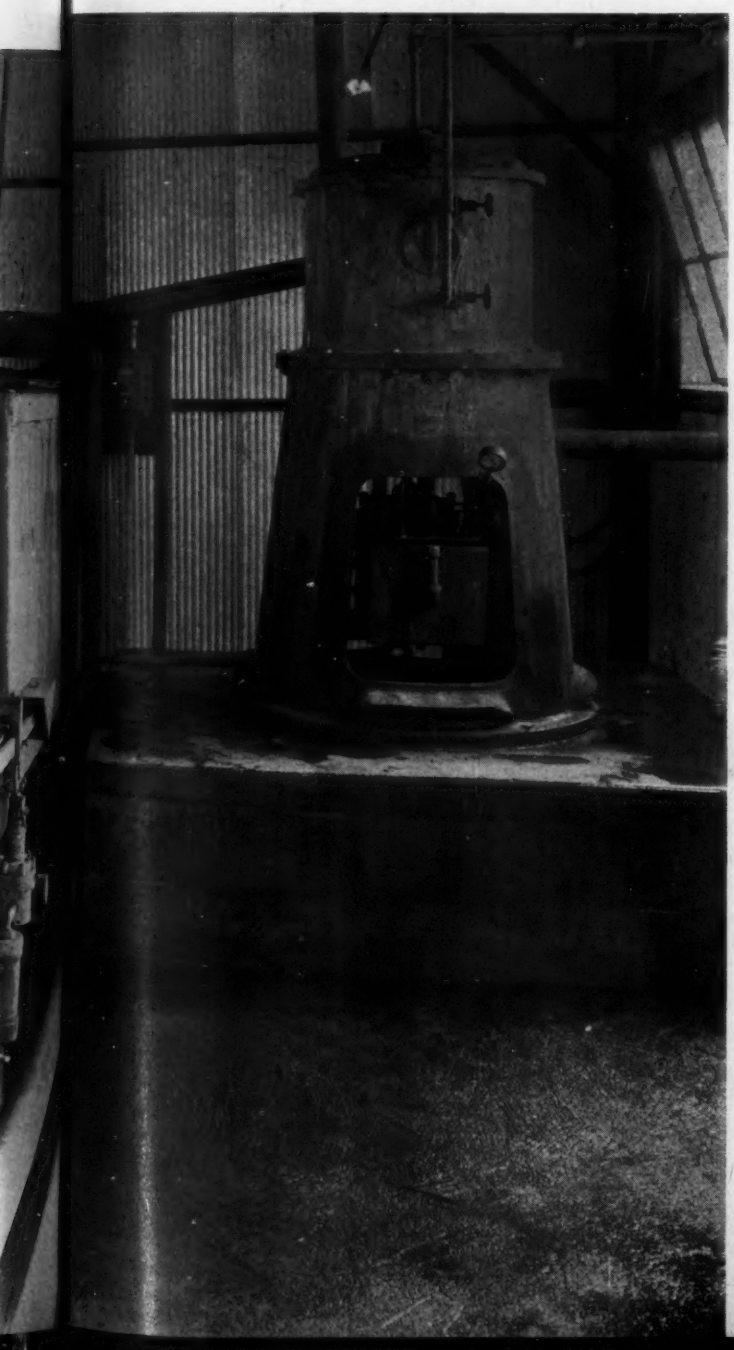
Centrifuge and regenerator in operation at Globe Oil & Refining Company's McPherson, Kansas, refinery.

Naphtha Recovery and Doctor Regeneration

Cuts Costs in Chemical Treating

CARL W. BERGER
Chief Chemist, Globe Oil & Refining Company
McPherson, Kansas

RECOGNIZING the opportunities for savings and for improvements in the conventional plumbite recovery operations, Globe Oil & Refining Company, (Kansas) of McPherson, Kansas, has installed, and operated successfully for four months, a unit of the Bayway Combination Centrifuging and Regenerating Process erected by Bayway Engineering Company.



The unit consists of one special demulsifier, and one mechanical spent doctor regenerator. The demulsifier has an individual built-in, explosion-proof 2-horsepower motor and is designed for an effective feed rate of 5 to 7 barrels per hour. The regenerator has an individual, built-in, explosion proof, 15 horsepower motor and is designed for an effective regenerating rate of 12

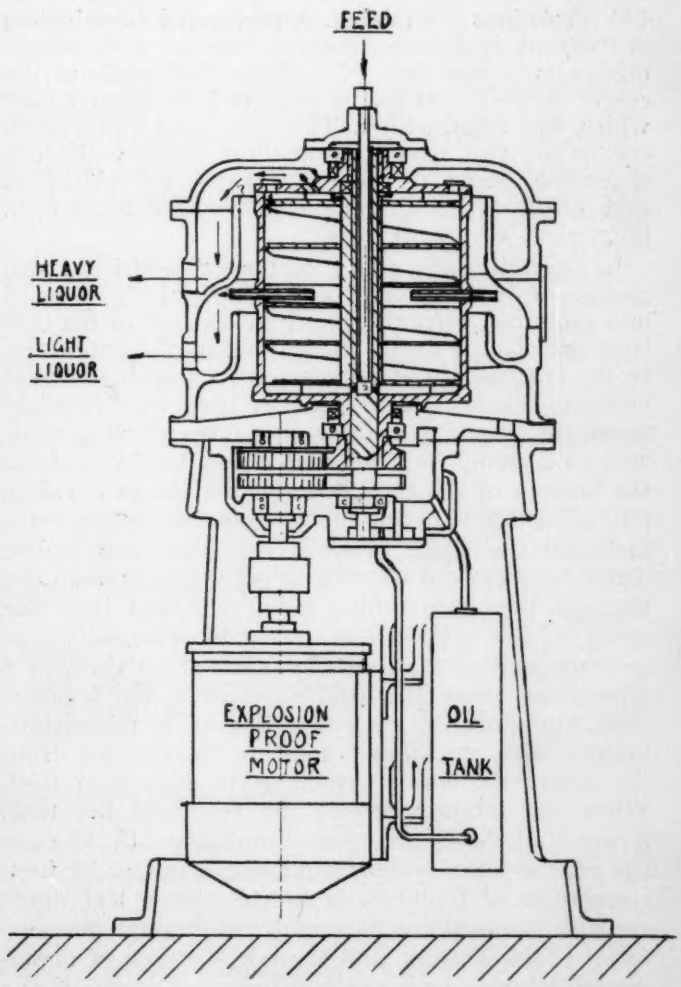


FIGURE 1
The demulsifier is a continuous bowl centrifuge which operates at a speed of 1250 R.P.M.

barrels of solution per hour to contain 8 to 10 pounds of soluble lead per barrel of solution.

The demulsifier is a modified continuous solid bowl centrifuge operating at a basket speed of 1250 revolutions per minute, and is shown in detail in Figue 1. (REFINER, Vol. 13, No. 3, March, 1934, Page 88, "Recovery of Naphtha from Spent Doctor Solution"). In operation, the feed is forced into the bottom of the bowl and gradually flows upward. The lead sulphide which settles in teh bowl is caught up by the blades of a screw operating at slightly different speed from that of the bowl, and moved slowly upward, being freed of naphtha in the process by the centrifugal action. The naphtha, being lighter than the caustic and lead sulphide, flows toward the center of the bowl where it forms a vertical layer and is trapped off to the gasoline discharge through four equally spaced nozzles. The caustic and lead are thrown toward the outside of the bowl by centrifugal action, and upward by the screw blades and find egress through a baffle and slot near the top of the centrifuge. The baffle is so constructed that only caustic and clean sulphide is discharged, holding any emulsified material in the bowl until broken.

The regenerator consists of a shallow, flat bottom tank in the center of which sets the special mechanism of the unit. Essentially, the latter is a suspended, motor-driven rotor surrounded by a cylindrical stator secured to the bottom of the tank and surmounted by a sleeve. The speed of the motor is 490 revolutions per minute. A perforated false bottom of the tank is equipped near the center with radiating ducts in the form of a clover leaf while at the center of the clover leaf is a larger hole directly over which the rotor whirls. The rotor and stator each consist of two cast iron annular rings with pipe spacers to separate the rings. Pipes are placed in such position that the openings between them form long, narrow vertical slots.

In operation, the spent doctor, or centrifuge discharge of lead sulphide and caustic, is introduced into a narrow, vertical channel on one end of the tank from which it is partly drawn and partly gravitates, to the bottom of the tank proper, beneath the false bottom. When enough feed has been introduced to cover the top of the stator slots, the whirling rotor acts as a pump impeller and draws liquid up from the bottom of the tank through the center opening, forcing it out between the pipe spaces on the rotor and into the space between the rotor and stator. Then, by means of its own velocity it is thrown out through the stator slots, being whipped into fine spray in the action. The action likewise creates a vacuum, pulling air from the atmosphere through a pipe rising above the level of liquid in the regenerator. The design is such that this air is mixed intimately with the doctor solution discharging from the stator, the whole assuming the form of a mist. When the mixture strikes the liquid in the tank, larger air bubbles are formed and pass off. The entire regenerating system is made continuous by first circulation of liquid back to the clover leaf ducts through the feed compartment and through the perforated false bottom, and second, overflow of regenerated solution to a sump provided. Details of the regenerator are shown in Figure 2.

The complete installation consists of the two units described above together with adequate doctor settling, circulating and storage tanks, doctor transfer pumps, and storage facilities for the recovered gasoline. At this plant very little in extra equipment was needed besides the centrifuge and the regenerator, the remainder being already present in the form of conventional recovery equipment.

One 200-barrel, cone bottomed tank (Number 5 in Figure 3) is used for circulating naphtha-free doctor through the regenerator. Consequently, the sodium plumbite strength in this tank would continue to build up indefinitely were it not for two further operations.

The first is that spent doctor emulsion from the treating plant is continually passing through the centrifuge, losing its percentage of naphtha and discharging also into the regenerator along with material circulating from Number 5 tank. In practice, spent doctor emulsion is collected in tanks 1 and 2 and pumped slowly through the centrifuge.

The second reason that Number 5 tank does not build up sodium plumbite strength indefinitely is that it is constantly overflowing finished doctor solution from near the top into tanks 3 and 4 for storage.

The entire system is controlled by intermittently checking litharge and caustic strength on Number 5 tank. Thus if the litharge strength becomes weak, more lead sulphide in the form of centrifugal spent doctor is pumped from 1 and 2 tanks. If the litharge strength becomes too high or the presence of excess unoxidized lead sulphide is noted, the centrifuging operations are slowed down. Caustic strength in the doctor can be increased when desirable by adding caustic at any one of several points, No. 5 tank usually being the recipient. In the manner described, uniform doctor solution can be maintained at all times or the strength varied at will for special purposes.

At no point in the cycle are temperatures of over 120°F. carried on the doctor solution. During the summer months, no steam at all is used, while in the winter only a little is necessary. It has been demonstrated effectively that heat is unnecessary for doctor regeneration after the emulsifying naphtha has been centrifuged out, and although the unit will operate at any temperature, trial runs at high temperature have not increased the efficiency by any measurable degree. Doctor solution emerging from the end of the system is cool and ready for immediate use.

Most of the outstanding advantages of such a system for doctor recovery are obvious and need not be discussed at length. The doctor reclaimed is superior to that furnished by the conventional steaming and blowing system. The strength is uniform the gravity or weight uniform, and it is free of emulsion or entrained, off-colored naphtha. Troubles encountered previously, such as fresh gasoline being thrown off color by regenerated doctor, entirely disappeared on the advent of the Bayway process. Less emulsion trouble and gasoline entrainment in spent doctor were enjoyed. Recovery operations were speeded up to the extent that finished doctor solution is always available and the treating plant need no longer wait occasionally for chemicals.

The mechanical nature of the operation removes

much of the personal element from making doctor solution and consequently eliminates errors arising from manual control. It is beneficial from a safety standpoint, the hazards from boiling over chemical tanks being removed, and the danger of fire resulting from gasoline evaporated from steaming doctor solution is avoided.

The disadvantages encountered with the system have been entirely too few to compensate for the advantages. It had been considered possible, because of the nature of the installation, that break-downs might occur, and for that reason, the old air and steam coils in the doctor tanks were retained. However, during four months continuous operation, only one short shut down was necessitated by the equipment. This involved the replacement of a bronze bearing in the centrifuge which had not been getting lubrication properly, an assembly fault easily corrected.

If the lead sulphide charge to the centrifuge is too heavy (contains too much solid material) the centrifuge may plug up and get out of balance, causing vibration. Provisions are made for introducing a stream of water or caustic into the machine while in motion to loosen and remove the solids. This is done once or twice per day as a matter of prevention and entails no loss of materials, and only a few minutes for the procedure.

The regenerator requires no attention at all except as the operator wishes to change specifications on emerging chemicals. It is provided with a sump on the discharge end controlled by a constant leveling float which actuates the steam pump circulating regenerated doctor solution back to storage.

The electric power necessary to operate the two motors involved is practically negligible, being an insignificant fraction of the cost of steam and compressed air, in the conventional doctor-recovery plant. The air supply to the regenerator comes, of course, from the atmosphere.

At the Globe plant, the installation has failed to come up to two expectations in its first four months operation. Both are a result of lack of capacity. It was expected that it would not be necessary to centrifuge all of the spent doctor solution; in other words, that some separation of clear liquid would occur in the spent doctor tanks provided for the treating plant to drop used chemicals into. Had this been true, the clear liquid separating could have been pumped to storage directly and its lead percentage built up by adding strong regenerated doctor solution. The expected separation, however, did not occur and it was found necessary to run all spent doctor through both the centrifuge and the regenerator. It is possible that on a sweeter crude such separation would have occurred, and it is also possible that at a later date this may be accomplished at this plant.

It was further expected that the finished doctor would always be entirely clear and free of suspended solids. Actually, the doctor carries 1 to 3 percent of finely divided lead sulphide, not enough to be harmful to the treating system, but enough to give the chemicals a dark color. Doctor tanks at the plant have not been cleaned of old sulphide since three or four months prior to the installation of the process, and it is hoped that such a cleaning (which had been periodic prior to the installation) might entirely clear the finished doctor.

The most impressive feature of the system is the dollar and cents savings made possible by its operation. Regardless of the other benefits, any successful system in the refining industry today must show a quick pay-out before it is even considered. It has been recognized for some time that measurable gasoline losses occur during sweetening operations, and various estimates have been placed on the extent of these losses. Actual operating data is now available

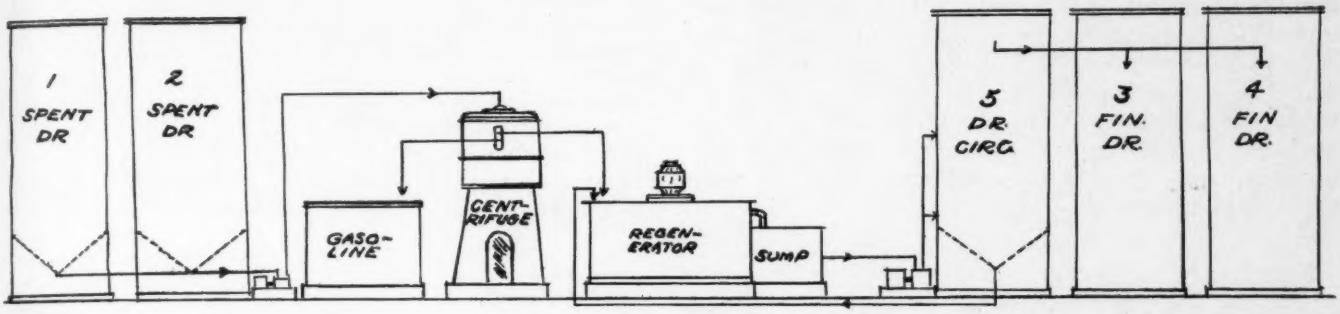


FIGURE 3

Flow chart of the Bayway combination centrifuging and regenerating process as installed at the McPherson, Kansas, plant of the Globe Oil & Refining Company (Kansas).

TABLE 1

	Conventional Costs	Bayway Costs
Chemical Consumption—Pounds per barrel treated:		
Litharge	$ 0.0610	$ 0.0118
Caustic Soda	0.1060	0.1191
Sulphur	0.0415	0.0421
Cost of Chemicals—Per barrel oil treated:		
Litharge	$ 0.003721	$ 0.0007198
Caustic Soda	0.002915	0.0032753
Sulphur	0.000863	0.0008752
	$ 0.007499	$ 0.0048713
Total Chemical Costs—(Corrected to same throughput)	$6,851.67	$4,476.42
Barrels Gasoline Recovered	.....	3,713
Percent Gasoline Recovered—Per barrel total products treated	.....	0.46
Gallons Gasoline Recovered—Per barrel doctor reclaimed	.....	9.180
Value of Gasoline Recovered—At $0.0325 per gallon	.....	$5,068.87
Four Month Saving:		
Chemicals saved	.....	$2,375.25
Gasoline saved	.....	5,068.87
Total	.....	$7,444.12

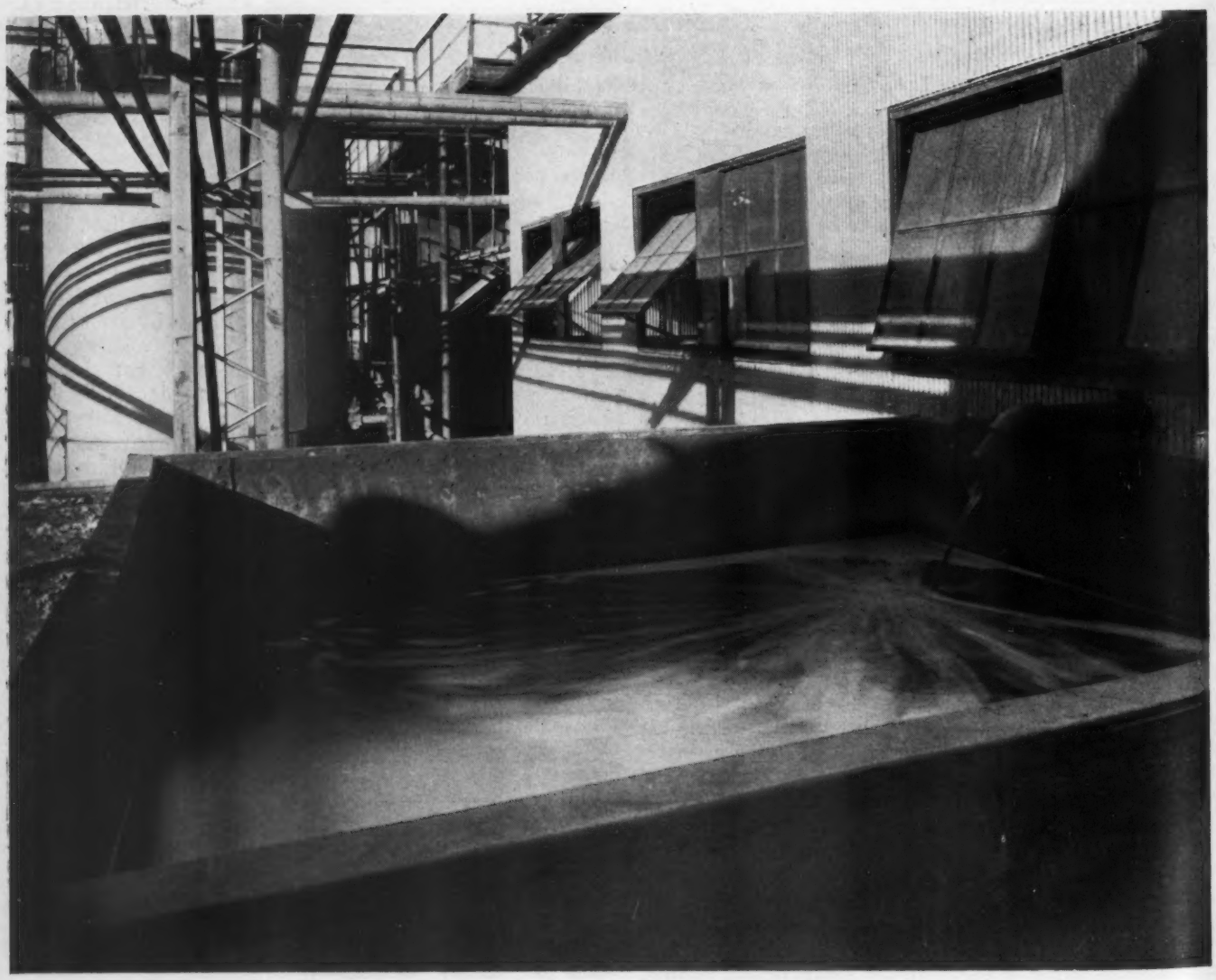
and should be pertinent information to the industry. The data covers, of course, only conditions extant at the Globe plant; still it is probable that similar conditions exist generally, the variable factors being largely matters of relative sourness of stock and efficiency of the plant sweetening system.

An interesting tabulation of data is given in Table 1. Under "conventional costs" are listed figures derived from a four-month operation of the sweetening system just prior to the Bayway installation, while under "Bayway" costs are listed the comparative figures for the four-month period subsequent to the installation.

The savings arrived at above, $7444.12 for four months operation, cover only actual chemical savings and gasoline recovery. Steam, air, and other savings have not been included for reason that accurate figures were not available, but it is conservatively estimated that total savings would amount to at least $25,000 per year on this plant. The all-important pay-out question is therefore only a matter of a few months.

Some objection may arise to the figure of $0.0325 per gallon listed for the value of gasoline recovered. Tests on the recovered material show an average of 95 percent boiling below 437° F., with an average end point of 462° F. The gasoline is straw in color (approximately — 22 Saybolt), sweet, and non-corrosive. The odor is good and the gum not excessive. It could reasonably be added to refinery gasoline direct, but is re-run by preference at this plant. The price set on it in the compilation was arbitrary but certainly conservative.

In conclusion, it may be pointed out that if proof were needed that the conventional plumbite sweetening operation is a wasteful step in refining, then the savings made possible by the simple modifications described in this paper furnished that proof. (REFINER, Vol. 15, No. 7, July, 1936, Page 255, "Economies in Doctor Treating.") There has been no intent to endorse or recommend the particular regeneration process described to the omission of any other sweetening or doctor recovery system, but rather to compare its observed plant operating data with those of the conventional plumbite system.



Naphtha discharge from the centrifugal demulsifier. Doctor tanks in the background.

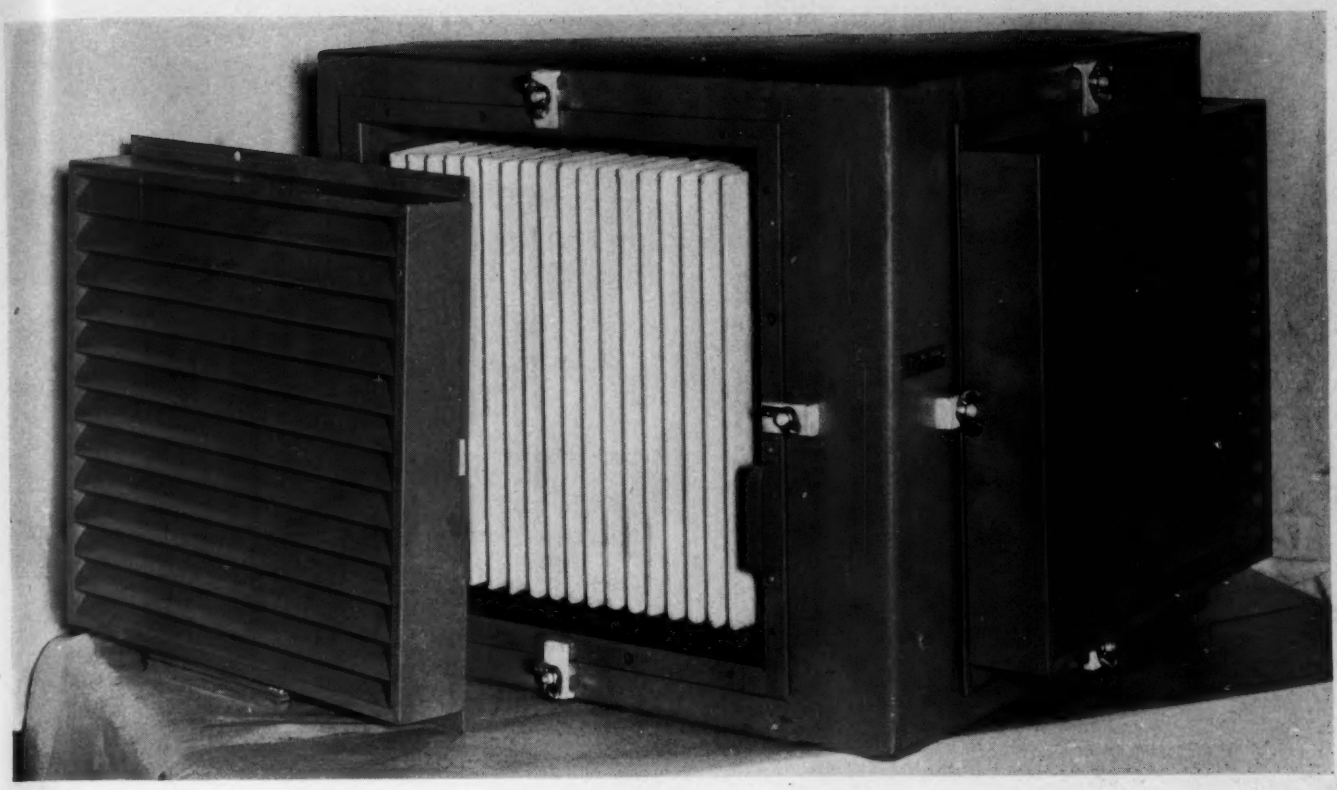


FIGURE 1
One type of filter for mounting directly on air intake pipe of engine or compressor.

Air Filters in Oil Refineries

E. KUNDIG
Coppus Engineering Corporation

INCREASING interest is being shown in air filtration by the oil refineries and oil refinery consulting engineers. The applications of air filters in this field are numerous and of varied nature.

It is easy to understand that dust in high concentration, as encountered during dust storms, is ruinous to most any equipment exposed to the atmosphere. A closer study however shows that even the microscopic dust particles in normal air are harmful to machinery, such as oil, gas and Diesel engines, electric motors and generators.

There is hardly a stationary internal combustion engine or large air compressor in service today in the oil field not protected by some kind of air filter.

The most common type of installation utilizes some standard make and size of air filter mounted directly on the air intake pipe of the engine or compressor. A typical filter of this type is shown in Figure 1. Weather louvers are added in front of the filter cells for outdoor installations in order to protect the filter medium from the elements. In Figure 2 is shown an outdoor installation of four air filters on two 1300-horsepower twin-tandem gas engines.

In what is considered normal atmospheric air, surveys show that there are about 4 grains of dust in every 1000 cubic feet of air. The fact that the human eye cannot see these dust particles does not disprove their existence. Ninety-seven percent of this dust consists of particles varying from 1 to 3 microns and considering that 1 micron is equivalent to 0.0004 inches it is not surprising that the human eye cannot see them. Most of these particles are silica and carbon.

How does this fine dust affect the operation of an engine or air compressor? It is well to recall that there are 4 or more grains of dust in every 1,000 cubic feet of so-called average clean air and that 7,000 grains are equivalent to one pound. Therefore, an engine of, we shall say, 150 horsepower, taking in approximately 1,000 cubic feet of air per minute will,

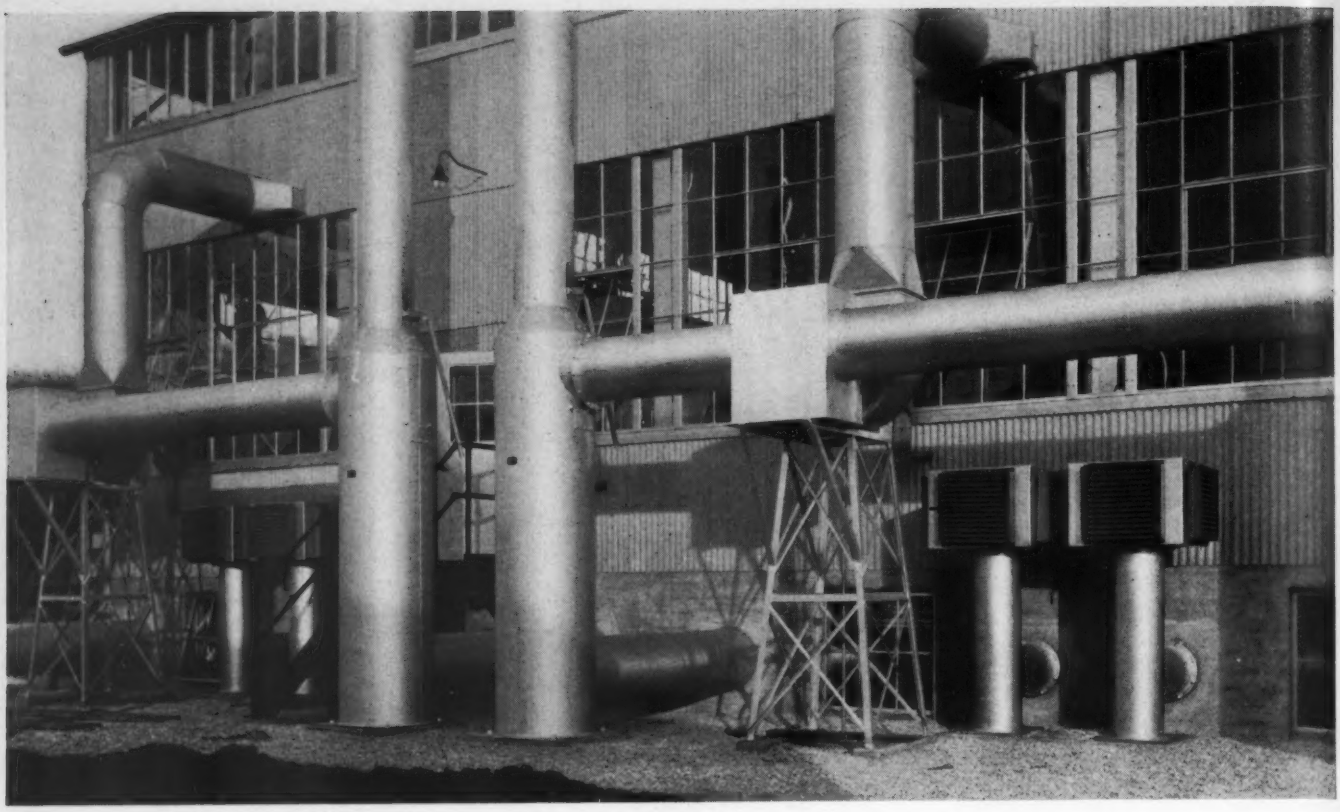


FIGURE 2

Out-door installation of air filters on two large twin tandem gas engines.

within 30 operating days of 8 hours each, draw in a total of 14,400,000 cubic feet of air and with it about 8½ pounds of this fine abrasive dust. This dust hastens the wear of valves, cylinders and liners and destroys the body of the lubricating oil.

By keeping this fine dust out of an engine or compressor up to 75 percent savings are assured in cost of upkeep and in preservation of the lubricating oil, not to speak of the generally prolonged life of the machine.

When selecting an air filter for this type of service, it is essential that the filter selected is capable of filtering these very fine particles out of the air.

For electric motors and generators using forced-air cooling or operating in dust-laden air, it also is of importance that the air be filtered before it reaches the commutator or windings.

If the motor or generator uses an air-circulating fan with sufficient capacity and suction to overcome the added resistance of air filters the filter units are installed in a duct leading from the filter bank to the electrical unit. Depending on the local conditions either room air or outdoor air is drawn through the filters. Where oil vapors are present within the plant, outdoor air should be used in order to keep the oil vapors from accumulating on the filter medium.

Air filters employing a dry-type medium should be selected. Oil-coated air filters may give off some of their own oil used as an adhesive medium, and it is important to keep the motor windings free from oil as well as from dust and dirt.

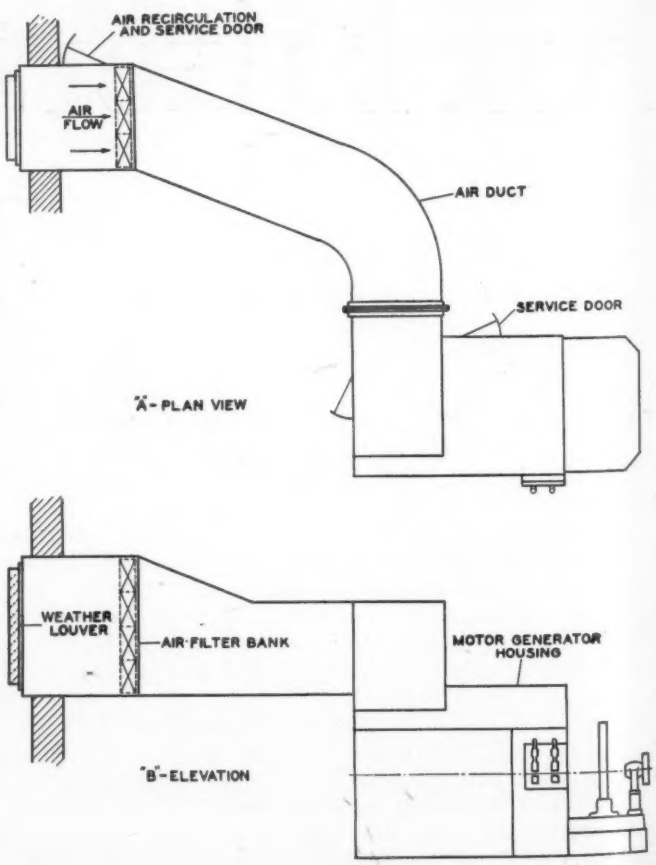


FIGURE 3

Filter installation details where electric motor or generator uses an air circulating fan.

An installation of this type is shown in Figure 3. As indicated, weather louvers should be used to protect the air filters from rain or snow, when outdoor air is utilized.

In many instances where open motors are involved or where the built-in fan of an electric motor or generator will not be sufficient to draw the air through filters, a separate fan is used. For such requirements a compact fan and filter unit as shown in Figure 4 is recommended. A unit of this type also will be found advantageous to serve motors or generators operating outdoors or in places not adequately protected from the weather elements.

Another method of assuring trouble-free operation of engines, compressors, motors or generators is to put the entire room in which they operate under a slight pressure of filtered air. For such purposes ventilator-filters are available, as shown in Figure 5. They consist of a ventilating fan equipped with air filter and can readily be installed in a window or in the building wall.

This method, however, is applicable only to comparatively small installations, especially when engines are involved. Large engines always use air from outdoors as too much vibration is created within the building due to the pulsating air flow, if the air is taken from within the operating room. A large unit supplied with indoor air would also make proper heating during cold weather practically impossible as the heated room air would be used up by the engine. Outdoor air is also cooler, thus assuring a higher engine efficiency.

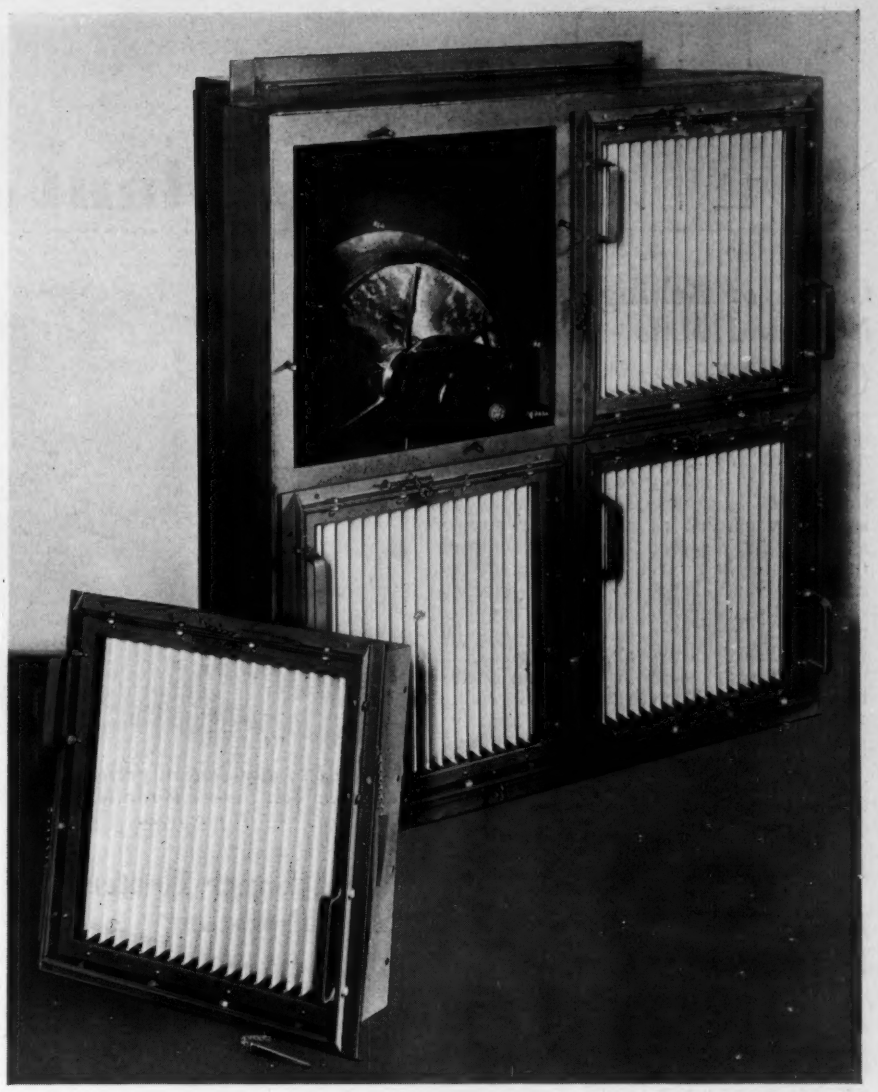


FIGURE 5

Ventilator-Filters for providing filtered air to rooms or buildings where machinery requires protection.

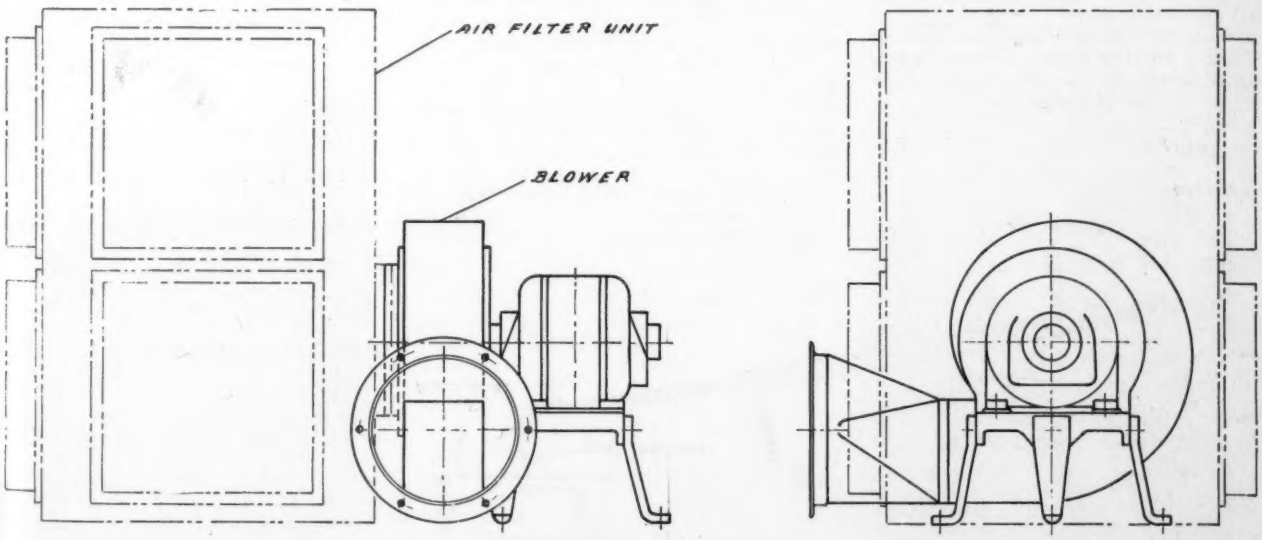


FIGURE 4

Installation details for use of separate fans for forcing air through filters.

IDEAS to help plant efficiency...

Conveyor Belting Makes Non-Skid Mats

CONVEYOR belts which have finished their useful life as carriers of material furnish the stock from which, with but a mallet and chisel, may be cut any number of resilient, safe floor mats.

Simply by blocking off the old belt in the desired lengths and laying out on its surface a pattern as intricate or simple as may be selected and then cutting through the belt on the marks, a safety non-skid tread is provided, with gaps to care for the usual dust and dirt from foot travel. The mat thus fabricated may be washed, hosed down, or left exposed in weathered spots with little or no disintegration and will withstand a surprising amount of interdepartmental trucking.

Mats made from old conveyor belting are especially suited to laboratory use, as they are practically acid-proof; and also find wide application as standings in front of electrical control panels due to their effective insulating properties.

Longview, Texas. ELTON STERRETT.

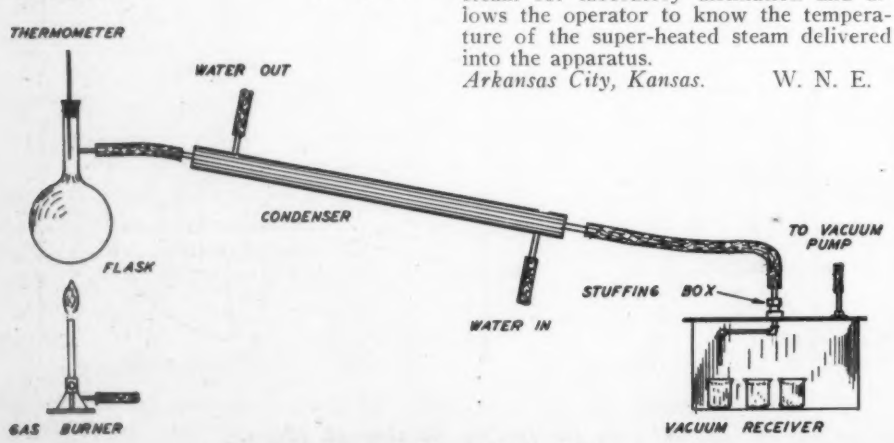
Punched to any desired pattern, this old conveyor belt makes a resilient, durable floor mat.

Laboratory Vacuum Distillation Apparatus

A LABORATORY vacuum distillation apparatus which can be easily and cheaply constructed is shown. The condenser is made from 1-inch pipe. The vacuum receiver is a 12-inch Pyrex Oceco look-box glass. The top and bottom of the receiver is ¼-inch steel plate. Twelve 100 c.c. beakers or 8—250 c.c. beakers are arranged around the inside, and by turning by hand the ⅛-inch pipe connections, 12 cuts can be taken during the distillation without interrupting the vacuum. The stuffing box can be made by using a discarded ½-inch valve.

A ring burner gives a smoother distillation than a Bunsen burner. Heavy rubber tubing connects the ¼-inch nipple on the condenser to the ⅜-inch nipple in top of the receiver.

Shreveport, La. A. W. T.



VACUUM DISTILLATION APPARATUS

Steam Super Heater For Laboratory

IN laboratory steam distillation it is desired to know the temperature of the steam, a convenient way of heating the steam and also a desirable means of delivering it into the still.

This set up is composed of a small sand bath large enough to hold enough sand to cover a 100 c.c. round bottomed flask. The flask is fitted with a cork stopper which has three holes in it, one for the steam to enter, one for the escaping steam, and one for the thermometer.

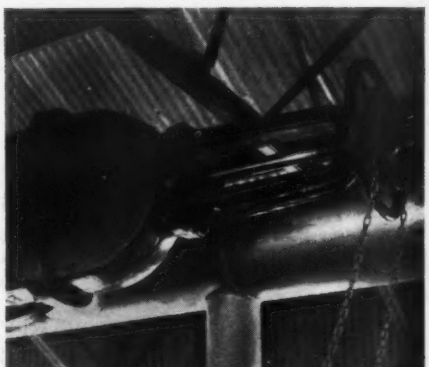
In making the delivery tube to the still, if it is made from one piece of glass tubing it will be more convenient for it is hard to hold a connection on glass at the temperature of super-heated steam.

This apparatus is designed so that it may be constructed with a minimum amount of table space and still large enough in delivering capacity to supply steam for laboratory distillation and allows the operator to know the temperature of the super-heated steam delivered into the apparatus.

Arkansas City, Kansas. W. N. E.

Control of Gas to Compressors

BECAUSE of surges of large volumes of gas produced at times in East Texas, it becomes necessary to control intake to engines rapidly if they are not to be overloaded. Gilliland-General Gasoline Company, near Kilgore, installed a block valve from the intake header to the suction of the engines, and in addition made it easily and quickly opened or shut as necessity arises. The gate was placed in a line supported above the compressors, too high for convenience in reaching from the floor, so a wheel from a chain hoist was brazed to the wheel of the gate, with the hand chain placed over



Quick open and shut gate for control of gas from the field to the compressors.

the hoist wheel. All that the operator needs to do when controlling the section of the engine room served by this blocked line is to manipulate the chain to open or shut the valve without running for a step ladder. The chain is looped over a convenient hook attached to the engine room wall so that it may be removed easily and quickly.

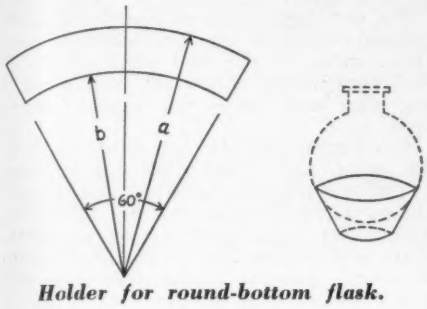
Removing Moisture for Laboratory Purposes

MOISTURE is readily removed from any of the lighter petroleum fractions for all laboratory purposes by using a funnel and absorbent cotton. Simply place the cotton in the funnel, press it down firmly and filter. This method works as well under vacuum as it does under atmospheric pressure. The fine particles of suspended moisture cling together and form droplets which pass through the funnel and fall to the bottom of the receptacle. Therefore, on the same type of liquid, one charge of cotton will last indefinitely. The advantages over filter paper are readily seen.

Longview, Texas. W. S. CAZORT.

Holder for Round Bottom Flasks

IT IS a problem to support large round-bottom flasks so as to avoid spillage and breakage during weighing operations. When the flask contains hot still residue which must be cooled before pouring it is especially important to avoid accidents.



Holder for round-bottom flask.

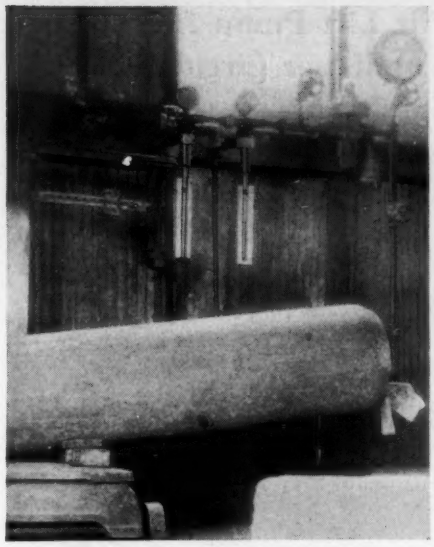
The accompanying drawing shows a device made of sheet metal which very conveniently solves the difficulty. It can be made to fit any round flask by making the radius "a" equal to or slightly less than the circumference of the flask. For flasks up to three liter capacity "b" should be three to four inches less than "a" to provide clearance. The ends may be joined by rivets or a lock seam.

Olean, N. Y. G. F. F.

Welded Joint Stiffeners

WHERE there is a possibility of welded joints needing protection, Phillips Petroleum Company has followed the method of welding fins across the seams so that additional stiffening is obtained. The usual practice is followed in joining the two pieces of piping, but after the seam has been completed, semicircular pieces of steel are welded across the seams from one piece of pipe to the other. Ordinarily four pieces are used for one joint, welded on both sides of the fins to prevent them becoming loosened from the pipe. The fins are usually cut with an acetylene torch from flat boiler plate, and have a notch removed from the side next to the pipe where they cross the welded seam.

Welded Joint Stiffeners.



Novel Ammonia Metering Installation

WHEN anhydrous ammonia is used to prevent metal corrosion in petroleum distillate streams the problem of accurately metering and controlling the flow is met. The photograph shows an efficient setup, and one that provides a double check on the amount of ammonia used. In the present installation two streams are supplied with ammonia from one cylinder, using two separate ammonia flow meters. It will also be noticed that a reducing valve is used between the cylinder and the meters proper. This precaution is deemed necessary due to the fact that if the full cylinder pressure were exerted on the glass manometers they would probably rupture. The schematic diagram shows two valves on the lines to the distillate streams. Each of these is used to maintain the exact back pressure necessary for the correct indication on the meter. The pressure on the low side of the regulator is held at approximately 35 lbs/sq. in. The ammonia cylinder is placed on a set of 500 lb. platform scales. By means of this the consumption over any period of time may be read.

HAROLD BOTTOMLEY.

Arkansas City, Kansas.

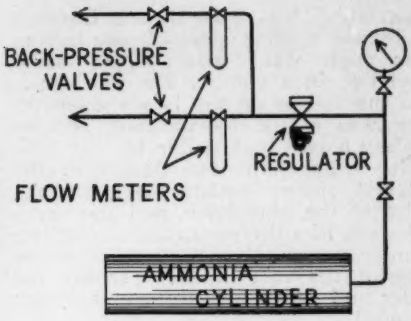
Bleaching Powder Mixer

FOLLOWING the inauguration by Carter Oil Company of its "Cash Your Ideas Club," an improvement was developed by one of the employees which prevents the waste of chlorinated lime by high winds picking it up when changing it from the drums to the chemical kettle.

The kettle, or chemical mixing drum, is a horizontal vessel which was equipped with a large opening in the upper side through which the powders were being shoveled through the hopper. Connections had been made on the upper side so gas could be introduced for pressure used in charging the treating columns with the chemical.

The operator now fills the horizontal chemical vessel to the required level with fresh water as in previously used methods of mixing, but instead of shoveling the powder into the tank through the hopper, it is drawn in by vacuum. A small pipe line is connected to a steam pump at one end and to the top of the tank shell at the other, approximately 18 inches above the water level. By using an extension nipple which reaches about half way into the mixing tank, to which a large hose is connected, the vacuum placed upon the tank by the suction of the steam pump, pulls the powder into the tank and below the water level.

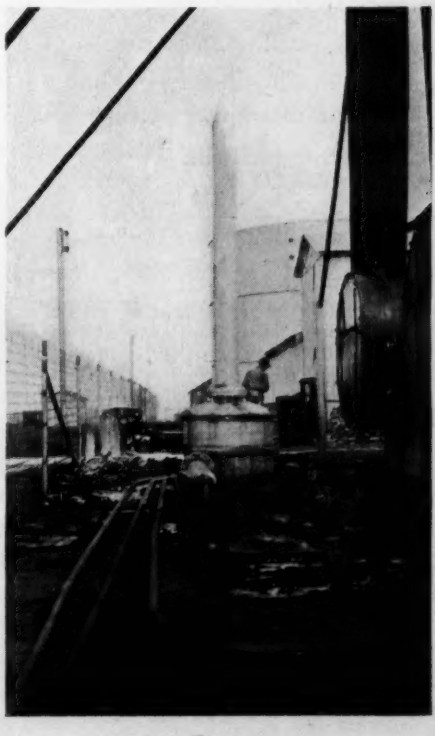
J. C. A.



AMMONIA METERING INSTALLATION

Boiler Blowdown Muffler

IN the Fairfax, Oklahoma, plant, Skelly Oil Company has erected a boiler blowdown muffler and waste water accumulator that not only prevents excessive noise of such operations, but effectually prevents any person from coming in contact with the hot water and sludge. Used equipment was utilized mainly for the unit by taking a cast iron gas engine muffler that had been removed from a plant as idle material. This was set between the boilers and the yard fence. The muffler was originally equipped with a tangential nipple with a flange for connecting the exhaust from the en-



Boiler Blow Down.

gine, which was used in this instance by bolting a short piece of pipe having four angle welds attached, by using steel two inch collars. The end opposite the flange on the larger diameter pipe was closed by welding, but including a two inch collar for the fifth boiler connection. The design of the original engine muffler prevents the noise of the blowdown, and the vertical stack lifts the steam above the surrounding equipment. A drain from the base of the cast muffler permits the water and sludge to run to a sump for disposal.

Rapid Calculating Method Of Gravity of Blending

IN blending two gasolines together for a given gravity, such as naphtha and casinghead, the following formula offers a convenient short cut calculation of the required percentages. When a person is caught out in the field or refinery without paper and pencil, this formula is, indeed, quite useful.

Formula I

$$\% \text{ of casinghead or lighter component} = \frac{(B-N)}{(C-N)} 100$$

where B = gravity of blend
N = gravity of naphtha or heavier component
C = gravity of casinghead or lighter component.

Example:

If gravity of CH is 80 degrees API, gravity of naphtha is 55 degrees API, and the required percentage of casinghead to give 60 degrees API gravity is wanted.

Then, % casinghead

$$= \frac{(60-55)}{(80-55)} 100 = \frac{(5)}{(15)} 100 = 33\ 1/3\%.$$

Conversely, it may be required to find the gravity of the blend when the percent of components are known.

The following formula will apply in this case:

Formula II

$$B = \frac{\%}{100} (C-N) + N$$

Example:

Using the data given in the first example:

$$B = \text{gravity of blend} = \frac{33\ 1/3\%}{100} (80-55) + 55$$

$$= \frac{1}{3} \times 15 + 55 = 60$$

It will readily be noted that by means of these formulas, the two examples given above could be easily solved without use of pencil and paper.

Following is the algebraic derivative of the above formulae:

$$\text{Let } x = \text{fraction of light component} = \frac{\%}{100}$$

$$\text{Then } Cx + N(1-x) = B$$

$$Cx + N - Nx = B$$

$$(C-N)X = B-N$$

$$x = \frac{B-N}{C-N} = \frac{\%}{100}$$

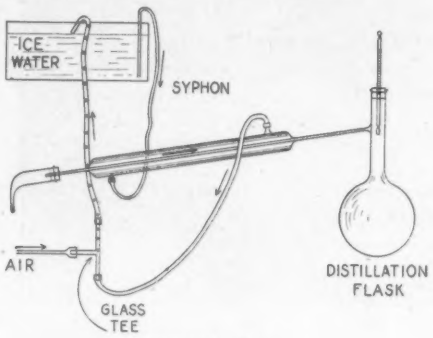
$$\% = \frac{(B-N)}{(C-N)} 100 = \text{Formual I.}$$

Formula 2 is derived from Formula 1 by solving for B.

El Dorado, Arkansas T. L. M.

Air Lift Pump for Condenser Circulation

THIS equipment is used where extreme cold water is required in the condenser of the distillation equipment. It is a convenient method for supplying water to the condenser, when tap water is not cold enough to condense the distillate.



Air Lift Pump.

A suitable container is filled with cracked ice and water, and a siphon is adjusted so that it delivers water to the lower end of the condenser. The water flows through the condenser and into an ordinary glass tee. The side arm of this tee is connected to the air line; and the other end is connected to a hose which leads back to the ice container.

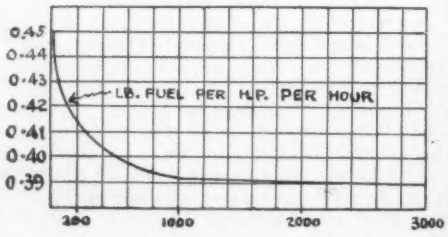
In operation of this equipment the siphon delivers the water to the condenser, thus flowing into the glass tee. A small quantity of air is forced through the tee, forming an air lift pump, which will again deliver the water back to the ice container. In this way, the water is circulated through the condenser and back over the ice, which keeps the condenser at a lower temperature than could be maintained by tap water.

W. N. E.

Diesel Performance

"IF we should install a Diesel engine how much fuel would it consume?" That question is often asked by oil men who are considering the use of a Diesel for power purposes.

In an effort to answer the above question definitely the writer has gathered data on fuel consumption by modern Diesels of numerous sizes and have developed the accompanying curve.



This curve tells at a glance what good Diesels are doing today, varying from the smallest sizes up to and including 3000 horsepower.

For instance if the requirements are very small—50 horsepower or even less—then figure on a fuel consumption of 0.45 pounds per horsepower per hour with a modern engine. In you need a 100 horsepower Diesel the consumption will be about 0.42 pounds per horsepower-hour. The curve shows that with increase in engine size the fuel consumption improves rapidly from the smallest sizes to 200 horsepower. From 200 to 1000 horsepower the improvement is less rapid. And from 1000 to 3000 horsepower the improvement is very slight being practically 0.39 pounds per horsepower per hour for all of the sizes in that range.

To determine the efficiency of any engine size, with any fuel, multiply the B.t.u. value of the fuel per pound by the number of pounds per horsepower per hour and divide the product into 2546.

For example if the fuel contains 20,000 B.t.u. per pound and you require a 500 horsepower engine, the chart shows that you must multiply 20,000 by 0.40, which gives 8,000 as the product. Now divide 2546 by 8,000 and it will be found that the engine will have an efficiency of 31.8 percent, which is a high efficiency as compared with most engines of other types. It means that 31.8 percent of the heat contained in the fuel will be converted into work. Even at 0.45 pounds of fuel per horsepower per hour, other conditions being the same, the efficiency will be 28.3 percent, which is a high efficiency.

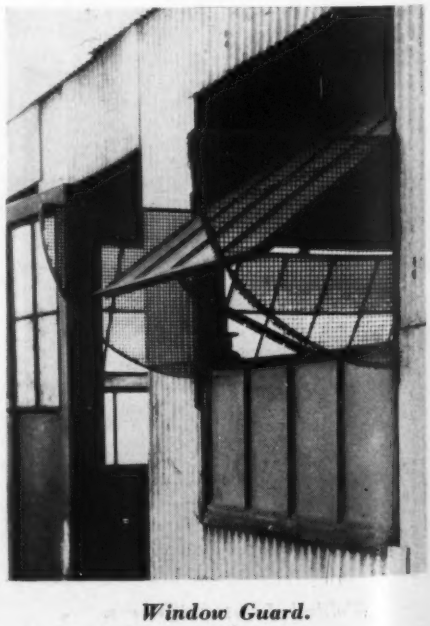
W. F. SCHAPHORST,
Newark, New Jersey.

Guard for Metal Sash Type Windows

WHEN windows of the metal sash swing-out type are open they present a hazard to the head and eyes of anyone passing them. The photo shows a type of metal guard made of heavy wire screen and ⅜" x 1½" strap iron that definitely cuts down the hazard of head injuries to passersby.

The strap iron is bent in the form of a quadrant of a circle and the wire screen neatly welded to the form. The finished guard is then welded or bolted directly to the building or window frame so that the sash is free to swing out to its normal open position.

HAROLD BOTTOMLEY,
Arkansas City, Kansas.



Window Guard.